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BLEACHING

BEING
A RESUMÉ OF THE IMPORTANT RESEARCHES
ON THE INDUSTRY PUBLISHED DURING THE
YEARS 1908–1920

BY

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PREFACE

The title of this book might be more accurately given as "Cellulose: Bleaching." To deal in one treatise with the subject of cellulose is impossible if a coherent mass is aimed at, and any attempt to deal with all the industrial aspects of the subject must end in failure. The subject is too big to admit of such treatment, but the time is probably now ripe to divide it up, thus enabling specialists in different branches to deal with these parts in a theoretical and practical manner.

The idea of this volume is not to give an account of the subject of bleaching, but to act more as a supplement to other published works, of which there are many, dealing with this branch of chemical industry. It is not meant for those who have no other books on bleaching. The principal intention of the author has been to discuss the important researches which have been published during the period 1908–20 bearing on the bleaching industry, and to present a record of work as a basis for the extension of research in the industry.

S. H. H.

July 1921.

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CHAPTER I

INTRODUCTION

The bleaching industry was founded on empiricism because then, as now, chemists had not accurately determined the nature of the substances composing the materials undergoing the bleaching. Raw vegetable fibres contain principally cellulose, waxes, proteins, pectic matters, colouring matters, and mineral matters, and all these constituents are of complex and undetermined constitution. The bleacher aims at separating the cellulose from the non-cellulose constituents of the fibre; he does this in the best and cheapest way he can, and with the least possible injury to the cellulose of the fibre. The methods he uses are the results of accumulated experience, and practical experience has taught him more than could possibly have been learned in the laboratory.

Chemistry has not yet fundamentally altered the processes used, and it is indeed remarkable that an industry founded on empiricism has changed so little in its character. A knowledge of chemistry cannot replace experience in the bleaching industry; there are many observations in practice which the chemist cannot adequately explain, and he must proceed cautiously while paying due regard to the teaching of experience. Chemists themselves are not very sure of their ground in discussing chemical matters affecting the industry; for instance, they still refer to oxycellulose and hydrocellulose, in spite of the fact that they have no test to distinguish definitely these so-called chemical compounds. Lack of definite knowledge on such points imposes caution on chemists dealing with cellulose industrially.

It is only reasonable to expect that the investigation of the constituents of textile fibres will have a large effect

on the textile industries in general, and on the bleaching industry in particular. It may, in fact, be presumed that the bleaching industry will be much affected by these investigations. It is for this reason that in this volume the industry has been reviewed in the light of these investigations, for it is perhaps in this direction that there is hope for the influence of chemistry introducing systematic order into the industry.

Work in textile chemistry is difficult because one is working with bodies of unknown constitution, which are unstable under certain circumstances and difficult to weigh accurately. For instance, on heating the cotton fibre, it only gradually assumes a constant weight, and it is more or less changed by the heating. Thus, at 100° C. the waxes are melted for the first time since their production in the cell, and the proteins are affected. If one tries to work with air-dry fibres, *i.e.* without drying them in a stove, the results are generally useless, because the weights are largely affected by the humidity of the atmosphere in which the weighings take place. It is only after very careful and accurately planned work that reliable results can be obtained. Moreover, experiments should be repeated at least once before conclusions are formed.

Textile materials as they come to the bleacher generally contain other matters than exist in the raw fibre itself. For example, cotton cloth generally contains a large amount of foreign matter, which has been added during the manufacture. In the sizing of warp yarns, flour, tallow, and other ingredients are used, and, on tearing a piece of cotton cloth, a fine dust is often given off owing to the presence of these added matters. The raw fibre is seldom bleached, and, further, during the preparation and spinning much of its impurities are removed. Fine yarns contain little or no admixture, and provide the best material for experiment. Conclusions formed from experiments with yarns can be applied to the bleaching of cloth, but some experiments with this material must also be performed to imitate the conditions in industry as much as possible.

As mentioned later, the author thinks the classification of the celluloses ought to be reviewed. He is not prepared

to attempt this classification himself, as he leaves it to those of more experience in this field. He himself is only concerned with one branch of the cellulose industry.

A few words might here be said about the words of the bleacher's vocabulary. He calls a bleaching solution made of a hypochlorite a "chemic" whether the hypochlorite be that of calcium (bleaching powder) or of sodium. In most cases, however, the term "chemic" refers to a solution of bleaching powder. A "sour" means a dip in weak acid. This acid might be hydrochloric or sulphuric acid, or a solution of nitre-cake. A "lye" or "ley" boil is a boil in a solution of alkali, either caustic or carbonate, or a mixture of the two; in some cases soap is added. A "scald" is a term applied to an alkali boil used for the goods after they have been treated with hypochlorites, whereas a boil is only called a "lye" boil if the goods have not been "chemiced." "Scouring" is a term usually applied to the whole treatment the cloth receives before being "chemiced." A protest might be made against the use of such terms in scientific writing, and perhaps too free use is made of works expressions by chemists, but in the case of the bleaching industry the use of these terms means a great economy of words; for this reason they are here retained.

CHAPTER II

CONSTITUENTS OF VEGETABLE FIBRES

Waxes—Proteins—Mineral matters—Pectic matters—Colouring matters—Cellulose.

This subject, which has of late received attention from technological chemists, is of great importance to bleachers, and it is safe to say that the cotton industry will be much affected by researches in this field. Bleaching is that branch of the industry which stands to gain the greatest benefit.

The actual composition of the growing plant is a tremendous subject, and the industrial chemist must look to researches in botany and biochemistry for guidance.

We are told that plants are made up of innumerable cells which are extraordinarily complicated in structure and consist of (1) the cell wall; (2) protoplasm closely applied to the inner surface of the cell wall; and (3) the cell sap. Protoplasm is the living substance of the plant, and in it there is a green envelope known as the chloroplast, a spherical body known as the nucleus, and the cytoplasm, a colourless mass in which the chloroplast and the nucleus are embedded. Cells may contain more than one chloroplast. The metabolic processes are primarily associated with the protoplasm, the operations of which are extremely complicated and little understood.

The cell wall contains carbohydrates of the cellulose group, mineral matters, and water, the mineral matters being distributed in minute particles throughout the carbohydrate. The cell sap contains water with dissolved organic and inorganic matter. The nucleus contains proteins and phosphorus.

Chlorophyll is a green colouring matter which is generally found associated with definite protoplasmic bodies to form chloroplasts. It is a secretion from the protoplasm. Light is required to produce the green colour, also oxygen and iron, although the latter element is not a constituent of chlorophyll. Chlorophyll is an extremely complicated substance which acts on the carbon dioxide of the air-producing carbohydrates and liberates oxygen. Its activity depends on the presence of certain mineral salts, potassium being said to be essential. Plants grown in darkness do not develop chlorophyll but etiolin, which is replaced by chlorophyll when the plant is brought into sunlight.

The solvent of the green pigment is probably some kind of oil; but as, during extraction by ether and other solvents, it undergoes decomposition, the determination of its chemical constitution is a difficult matter. Willstätter, however, has shown that chlorophyll has two components in about the same relative proportions, and only apparently differing in that one has one more oxygen atom replacing an equivalent of hydrogen in the other. Both are esters of a monohydric alcohol of high molecular weight, phytol, and yield on hydrolysis 30 per cent of phytol, together with a tricarboxylic acid which contains four pyrrol rings.

Magnesium is supposed to be the active principle of chlorophyll. By the action of acids and alkalis the products of chlorophyll are divided into two groups containing magnesium and not containing that metal. With alkalis hydrolysis to two isomeric tribasic alcohols takes place, and carbon dioxide is evolved. With soda lime a third molecule of carbon dioxide is evolved. Acids remove the magnesium, replacing it by two atoms of hydrogen, and this fact is of importance in bleaching. The yellow pigments of plants are carotin, an unsaturated hydrocarbon, and xanthophyll, an oxidation product of it. Both absorb oxygen when isolated.

Plants have been found to contain the elements hydrogen, oxygen, chlorine, sulphur, nitrogen, phosphorus, silicon, carbon, potassium, sodium, calcium, magnesium, and iron. The compounds in plants are very numerous,

the majority being by-products of metabolism, and most of these have not yet received exhaustive treatment.

The constituents of plants have been divided into the following groups:

(1) Organic acids; as oxalic, citric, etc.
(2) Glycerides of higher fatty acids—fats.
(3) Carbohydrates; mono- and di-saccharides, as dextrose and cane-sugar, and poly-saccharides, as starch and cellulose.
(4) Amido compounds—amido acids and acid amides.
(5) Ethereal oils.
(6) Resins.
(7) Alkaloids.
(8) Glucosides.
(9) Pigments.
(10) Proteins.

Water is contained in all parts of plants, and in estimating the constituents of plant products they must first be dried. This may be done in air, that is, at about 30° C. or at 100° C. At the latter temperature proteins are completely changed by drying, but fats, glucosides, tannins, and carbohydrates are not seriously altered. Proteins should not be dried above 30° C. Fibres dried at 100° C. are also found to be changed, *e.g.* in their dyeing properties, as mentioned on page 82.

The solvents usually used for treating plant products are the following:

(1) Ether or benzene, which extract oils and fats, ethereal salts of organic acids, resins, terpenes, colouring matters, chlorophyll, waxes, lecithin, cholesterin, hydrocarbons, essential oils, lipoids (an indefinite group of substances), etc.

(2) Alcohol, sp. gr. 0·85, which extracts tannins, glucosides, part of the sugars, etc.

(3) Cold water, which extracts dextrins, soluble carbohydrates not extracted by 0·85 alcohol, some proteins, nitrates, nitrites, etc.

(4) Sulphuric acid (1 per cent), which acts upon starch, proteins, etc.

The extracts decompose on keeping. The tannins and

most glucosides reduce Fehling's solution. Tannins occur in solution in the cell sap, but they must be separated from albuminoids or a precipitate would be produced. Lecithins are yellow wax-like solids with a peculiar odour. As regards glucosides it is found that the maximum of hydrocyanic acid obtains in the flax plant when the seedlings are 4 or 5 inches high. Raffinose occurs in cotton seeds. The amount of the resins and terpenes is usually small except in barks. Resins and allied bodies are formed by a peculiar process of degradation of the cell wall. They are products of metabolism as are also alkaloids, seeds, and aromatic substances. Alkaloids can sometimes be extracted by volatile solvents, but usually it is necessary to treat with lime to liberate the base and then extract. Betaine and choline occur together in *Gossypium herbaceum*, which is the principal source of the cotton fibre. There is much more nitrogen in these bases than in proteins.

Of the textile fibres which have been analysed the following examples have been selected from figures given by J. M. Matthews[1]:

[1] *The Textile Fibres* (Chapman & Hall, London).

[TABLE

	Cotton.					Flax.		China Grass.	Ramie.	Hemp.	Sunn Hemp.	New Zealand Flax.	Manilla Hemp.	Jute.		
	I.	II.	Surat.	American.	Egyptian.	I.	II.							I.	II.	III.
Cellulose . . .	91·15	91·35	91·35	91·00	90·8	82·57	71·5	78·07	66·22	77·77	80·01	63·00	64·72	64·24	63·05	61·74
Wax	0·51	0·40	0·40	0·35	0·42	2·39	2·37	0·21	0·59	0·56	0·55	1·08	0·63	0·39	0·32	0·45
Protoplasm and derivatives . . .	0·67	0·50	0·53	0·53	0·68	...	...	...	...	...	...	...	...	...	...	...
Aqueous extract .	...	...	...	...	...	3·65	6·02	6·47	10·34	3·48	2·82	21·99	0·97	1·03	1·63	3·94
Incrusting and pectic matters . . .	...	...	...	...	...	2·74	9·41	6·10	6·23	9·31	6·41	1·69	21·83	24·41	25·36	21·29
Mineral matter (ash) .	0·11	0·12	0·22	0·12	0·25	0·70	1·32	2·87	5·63	0·82	0·61	0·63	1·02	0·68	...	...
Water . . .	7·56	7·00	7·5	8·00	7·85	8·65	10·70	9·05	10·15	8·88	9·60	11·61	11·85	9·93	9·64	12·58

Bulletin No. 33, U.S. Dept. Agric., gives the following analysis of the cotton fibre:

	Per cent.
Water	6·07
Ash	1·37
Nitrogen	0·34
Phosphoric acid	0·10
Potash	0·46
Soda	0·09
Lime	0·19
Magnesia	0·08
Ferric oxide	0·02
Sulphuric acid	0·6
Chlorine	0·07
Insoluble matter	0·05

Approximate Constituents.

	Per cent.
Water	6·74
Ash	1·65
Protein	1·50
Cellulose	83·71
Nitrogen per extract	5·79
Fat	0·61

E. Knecht (*Journ. Text. Inst.*, 1911, **2**, 22-29) found the following extracts from cotton:

	Raw Cotton.			Cotton Yarn.[1]	
	Egyptian.	Bengal.	Texas.	American.	Egyptian.
Benzol extract	0·47	0·38	0·55	0·407	0·444
Alcohol extract	0·68	...	0·90	0·533	0·744
Aqueous extract	1·46	...	1·61	1·656	1·509
Ammonia extract	0·45	...	0·39	0·425	0·5
Formic acid extract	0·46	...	0·72	0·65	0·405
Hydrochloric acid extract	...	...	...	0·656	0·54
Total	3·52	0·38	4·17	4·327	4·142

S. H. Higgins (*Journ. Soc. Chem. Ind.*, 1914, **33**, 902) in extracting linen yarn found the following:

Benzol extract	1·68
Alcohol extract	0·49
Aqueous extract	2·03
Ammonia extract	3·27
Caustic soda (under pressure)	14·06
Hydrochloric acid	0·33
	21·86

[1] E. Knecht and W. Hall, *Journ. Soc. Dyers and Col.*, 1918, 220.

Knecht found the alcoholic extract, which was obtained in the order mentioned, that is, after the benzol extraction, was amorphous, very hygroscopic, and of a rich brown colour. The aqueous extract was similar to the alcoholic extract, brown and hygroscopic. The formic acid extract was mainly mineral. The alcoholic extract from Texas cotton contained 1·07 per cent of nitrogen, and reduced Fehling's solution strongly. Higgins found that the alcohol extract of linen was golden brown and hygroscopic. The water extract on evaporation yielded brown brittle scales. If the brown linen had been treated with all the reagents mentioned, and not successively as described, quite different results would have been obtained. For instance, alcohol removes most of the waxy matters taken out by the benzene, and sodium hydroxide removes a large proportion of all the non-cellulose constituents of linen. Linen cloth, boiled under pressure with water, gave up from 3·3 to 4·5 per cent of its weight to the water, and it was also found that the same cloth treated with hydrochloric acid in the original state gave up 1·10 per cent of matter. During the extraction with ether it was found that the wax was only taken out very slowly, and after prolonged extraction there was always some left which benzene removed (Higgins, *loc. cit.*). Barnes (*Journ. Soc. Chem. Ind.*, 1916, **35**, 1191) confirmed this observation during the extraction of Indian cottons. He found ether extracted from 0·188 to 0·618 per cent of matter from Indian cottons.

E. E. Stanford and A. Viehoever (*Journ. Agric. Res.*, 1918, **13**, 419-435) found that the internal glands occurring in the seeds and other parts of the cotton plant contain quercetin, probably as glucosides, ethereal oil, resins, and possibly tannins. They are surrounded by flattened cells which contain a red anthocyan pigment. The glands not normally exposed to light contain gossypol, and are surrounded by a layer of flattened cells which do not contain anthocyans. On exposure to light the gossypol is replaced by a glucoside of quercetin.

Waxes

The mode of formation of oils, fats, and waxes in plants is not thoroughly understood: in the case of glycerides, it

is not known whether the fat is produced from the fatty acid and glycerin in the protoplasm. Fatty oils occur in all cells, and it is doubtful whether there is such a thing as protoplasm free from fat. Fats and oils are frequently stored as reserve foodstuffs in plants, and waxes pass beyond the walls, forming a layer on the outer surface; ethereal oils are found deposited in cavities in leaves, stems, and other parts. The formation of fat is due to the decomposition of the protoplasm, oil drops being formed. Fat is changed into carbohydrates during the germination of seeds, and in ripe seeds starch is changed into fat. The chemistry of such changes is not understood, but the alteration of fat into carbohydrate is manifestly impossible without oxygen.

E. Knecht (*Journ. Text. Inst.*, 1911, **2**, 22-29) found on extracting raw Egyptian cotton sliver with benzene that 0·47 per cent of crude wax, having the appearance and consistency of bees-wax, was obtained. On treatment with petroleum spirit the crude wax was resolved into two constituents: cotton wax A to the amount of about 70 per cent soluble in the spirit, and cotton wax B insoluble in petroleum. Cotton wax A has a pale colour, melts at 66°-67° C. and consists for the most part of a true wax, containing besides some free fatty acids, small proportions of glycerides, and some hydrocarbons. Cotton wax B is a dark green, granulated but plastic substance, melting at 68° C., and containing very little free fatty acid. W. L. Balls[1] states that the cuticle of the seed coat is slightly waxy, probably from the same wax which has long been known to occur in the lint. Until this wax has been broken by the mutual swelling of the seed the absorption of water is difficult. E. Knecht and J. Allan (*Journ. Soc. Dyers and Colourists*, 1911, **27**, 142-176) found on repeatedly treating the first fraction mentioned above with boiling 96 per cent alcohol that 18·82 per cent of an insoluble wax of glassy appearance was left; it melted at 78° C., and had an iodine value of 11·28. The portion soluble in alcohol was more plastic; it melted at 62° C., iodine value 33·42. With alcoholic potash the wax was only slightly saponified, but using glycerin-caustic soda it

[1] *The Development and Properties of Raw Cotton* (A. & C. Black, Ltd., London, 1915).

was found to contain 47·5 per cent of unsaponifiable matter, melting at 67°-68° C. This product was acetylated and from it were obtained two hydrocarbons in crystalline form, one melting at 68·1° C., and giving on analysis figures agreeing closely with those for hentriacontane ($C_{31}H_{64}$), and the other melting at 70° C. and agreeing on analysis with the formula for dotriacontane or dicetyl ($C_{32}H_{66}$). From the acetylated alcohol a crop of crystals were separated on cooling its ethyl alcohol solution. They melted at 127·3° C., and the substance was evidently a phytosterol. An acid of melting point 74·4° C. (which was almost certainly cerotic acid) was separated, and also stearic and palmitic acids. The second fraction of wax melted at 68° C., acid value 4·03, and saponification value 83·3. The reddish-brown unsaponifiable portion melted at 63·4° C. Phytosterol was again isolated, and a crystalline acid, probably melissic acid ($C_{30}H_{60}O_2$).

Piest (*Z. angew. Chem.*, 1912, **25**, 396-399) stated that the "copper number" of cotton was increased by the presence of the cotton wax. This observation points to the presence of a reducing agent in the wax, probably corresponding to the aldehyde of linen wax mentioned by Hoffmeister (p. 13). Knecht has also pointed to the reducing properties of the non-cellulose constituents of cotton.

On extracting cotton with benzene, then treating with acid, washing, drying, and again extracting with benzene, the cotton yields more fat to the benzene (Higgins, *loc. cit.*). The fatty acid exists on the fibre as a magnesium soap; the acid dissolves out the magnesium and leaves the fatty acid for extraction by the benzene. The amount of this fat is about 0·05 per cent, that is, about 10 per cent of the amount of the wax originally extracted by the benzene.

The figures given by Knecht (p. 9) show a total of about 4 per cent of matter accounted for in the extracts, and as bleaching, that is, producing the pure cellulose, only brings about a drop of about 5 per cent in weight it is seen that this drop is largely accounted for in the steps given.

Hoffmeister states that flax wax melts at 61·5° C., and

has a sp. gr. of 0·9083 at 60° F. It consists of 81·32 per cent unsaponifiable matter and 18·68 saponifiable, of which 54·49 per cent is free fatty acid. The unsaponifiable portion has a melting point of 68° C., and contains ceresin, ceryl alcohol, and phytosterin. Caproic, stearic, palmitic, oleic, linolic, linolenic, and isolinolenic acids were found in the saponifiable portion. Bianchi and Malatesta (*Annali Chem. Appl.*, 1914, **1**, 297-302) found flax wax to have a sp. gr. 0·9980 at 15° C., m. pt. 68°-70° C., acid value 23-23·8, iodine value 17-17·5. The saponification value by the ordinary method was 111·9, but rose to 156-163 on prolonging the treatment up to 6 hours. The unsaponifiable matter (20-23 per cent) was a brittle brown substance of m. pt. 73°-74° C., sp. gr. 0·986, free from phytosterol, and consisting mainly of hydrocarbons. Hemp yielded 0·5-1·2 per cent of fatty matter of somewhat similar character to that obtained from flax, m. pt. 66°-67° C., sp. gr. 1·019, acid value 46-47, iodine value 22·2-22·8, and saponification value 187-192. It contained 11 per cent of unsaponifiable matter of m. pt. 60° C., sp. gr. 1·0022.

Hoffmeister also noticed in flax wax a small quantity of a volatile aldehyde-like substance, and Higgins (*loc. cit.*) plainly observed this substance by the coughing it produced on breathing the atmosphere in the neighbourhood of the heated ether extract of linen. The figures for linen given on p. 9 were for water-retted yarn. Dew-retted yarn gave up 0·92 per cent of wax to ether, and a further 0·27 per cent to benzene. It seemed possible that on continuing the extraction with ether long enough the matter which the benzene removed would also be dissolved out by the ether, but although this point was tested many times it was always found that, after the action of the ether, benzene extraction eliminated further wax from the yarn.

As in the case of cotton, Higgins also found that on extracting linen with benzene, then treating with acid, washing, drying, and again extracting, more fatty matter was taken up by the benzene, and magnesium was found in the acid.

The melting point of the wax lies between the boiling points of ether and of benzene, hence the hot benzene used

in the extraction melted the wax and dissolved it out very readily. The wax separated from the hot benzene on cooling. The wax extracted by ether was light yellow or light green; on melting, it became the same colour as the wax extracted by benzene. On solidifying, the wax fractured in a peculiar manner. Sometimes the wax was of a dark green colour, and the cloth turned from a greenish-brown to brown during the extraction. On removing the wax the cloth lost its peculiar smell. On using different solvents for the extraction, such as ether, gasolene, petroleum ether, and benzene, it was found that the lower the boiling point of the solvent the lighter the colour of the wax extracted. The darkening of brown linen and cotton cloths on heating is due to the melting of the wax, which changes in colour from yellow to brown.

Water-retted flax was found to contain from 1·57 to 1·95 per cent of wax; dew-retted flax about 1·19 per cent. This difference in the proportions of wax in the two fibres is interesting, since these waxy matters are supposed to be products of the decomposition of cellulosic bodies during the retting and other processes.

Jute yarn was found to give up 0·9 per cent of a greenish-brown, strongly smelling oil to benzene; the extracted fibre again had no smell.

Effect of the Extraction of the Wax on the Properties of the Fibres

Knecht conducted spinning trials with Egyptian cotton which had been deprived of its wax, and found that the dewaxed material behaved very badly in the drawing and spinning operations, giving an excessive amount of waste, irregular results, and showing a tendency to adhere to the rollers. Finer counts gave great trouble, and breakages were extremely frequent. In the loom used as warp the dewaxed thread was also troublesome on account of breaks, and the yarn spun from the dewaxed cotton was 24·5-27 per cent weaker than the ordinary yarn. On the other hand, the extraction of the wax from the ordinary yarn after spinning increased the

strength by 13 per cent,[1] while the addition of 2 per cent of paraffin wax to this extracted yarn decreased its strength again by 33 per cent. Substantive dye-stuffs gave lighter shades on the extracted cotton than on the ordinary cotton; methylene blue, however, gave darker shades on the extracted samples.

In the case of linen yarn Higgins found the following changes in strength:

	Breaking strength.
Original yarn	730 grms.
After ether extraction	790 „
„ benzene „	750 „
„ alcohol „	720 „

The ether evidently removed matter which caused the slipping of the fibres over one another, and benzene apparently extracted certain waxy matters, which had a consolidating effect on the fibres. Other tests with dew-retted yarns gave similar results, the greatest increase in strength being always produced by the solvent with the lowest boiling point, viz. ether.

Proteins

Proteins are most complex substances, concerning the molecular structure of which we know little. The proteins of seeds have been studied, but those occurring in the active cells and fluids of plants have not yet received much attention from chemists, principally because they occur in small quantities and are difficult to separate. Some proteins yield a small quantity of ash on ignition, but it is not certain that these ash constituents form part of the protein molecule: they are probably impurities very difficult to remove.

Proteins are closely incorporated with the protoplasm of plants, and the original construction of protein matter, like that of carbohydrates, seems to be carried out only by the vegetable protoplasm. It is produced in an unknown

[1] E. Knecht and W. Hall (*Journ. Soc. Dyers and Col.*, 1918, 220) found that American yarn increased 12·4 per cent in strength on extracting with benzene, and lost 4 per cent in elasticity, the figures for Egyptian yarn being 11 per cent and 9·9 per cent respectively.

manner from the nitrogen absorbed by the plant. In some cases protein is found in definite grains in the parts of plants. Plants accumulate a reserve of food, proteins and carbohydrates being constructed in excess of immediate requirements, and deposited in an insoluble form to relieve the cell sap. The sugar and proteins in soluble form are conducted through the parenchyma to the fibro-vascular bundles, the bast of which forms the principal path. It is during this passage that some of the carbohydrates and proteins are changed to the storage forms, for grains of starch are of frequent occurrence in different parts of the bast, and proteins can be observed in the sieve-tubes of the bast. The principal function of the bast is to form the pathway of translocation of the food material. These reserve deposits may be rapidly reabsorbed by the plant. Proteins may be accumulated as in seeds, or dispersed in an amorphous form in the substance of the protoplasm. In many cases amino-acids, as asparagin, may be detected in the sap of various cells. In cereal grasses the protein is deposited in layers, in some cases associated with oil.

Sulphur is a constituent of all proteins, and proteins are found in all protoplasm. Sulphur also occurs in plants as organic sulphides.

Phosphorus does not seem to be present in the ordinary cytoplasm, but it is undoubtedly associated with the nucleus. It is contained in the substance called nuclein to the extent of about 6 per cent. Phosphorus has not yet been proved to be a constituent of any of the seed proteins thus far studied, and small amounts of phosphorus apparently contained in some preparations of these substances have been found to disappear on purification by repeated precipitation. Phosphorus is probably present in the enzymes which are concerned in the digestive processes of the plant, and is also said to occur in chlorophyll. Lecithin, a complex fatty body containing phosphorus, is present in actively growing cells in many plants, and in a few plants phosphorus is said to be temporarily stored in the seeds. Phosphorus is absorbed by the plant as phosphate, usually as calcium phosphate.

Proteins are converted by enzymes into amino acids of definite compositions, and these substances are also found to occur in plants, *e.g.* asparagin.

Some proteins are soluble in water, some are insoluble; some are soluble in aqueous solutions of neutral salts. Nearly all are insoluble in alcohol or ether, but some are soluble in a mixture of alcohol and water (90 per cent alcohol). They all dissolve in strong mineral acids and caustic alkalis but are somewhat changed in the process.

Osborne[1] says that with dilute alkalis the protein is probably little changed by the extraction, and if the alkali is not too strong this can be used as a method of separating proteins. Most seed proteins are very incompletely coagulated by heating their solutions even to boiling, and many of them are not coagulated at all under these conditions: alkaline solutions cannot be coagulated by heat. Proteins dissolved by alcohol are unchanged.

Edestin extracted from hemp seed by salt solution gives a slightly acid reaction to litmus, but to lacmoid it reacts alkaline. Vegetable globulins show a distinct acid reaction to phenol phthalein, therefore proteins show both basic and acid properties. Proteins are precipitated by adding neutral salts to their solutions if of sufficient concentration. Saturated ammonium sulphate will precipitate all proteins except peptones. Proteins may be purified by dialysis. Coagulation may be brought about by heat, alcohol, or ferments. Amino acids are fermented by yeast with the production of alcohols.

The antiseptic action of mercuric chloride is probably connected with the formation of insoluble salts with proteins.

Mineral Matters

As previously stated plants contain a large number of elements in their composition. Of these, potassium, lime, magnesium, sulphur, phosphorus, and iron are found to be essential. Sulphur is an essential constituent of all proteins, as also is nitrogen; phosphorus is contained in some proteins. Potassium can sometimes be replaced to a

[1] *The Vegetable Proteins* (Longmans, Green & Co.).

large extent by sodium. Magnesium appears to be always a constituent of chlorophyll, and it cannot be replaced by any related alkaline earth. Lime does not take part in the living cell, but occurs in older organs and especially in leaves. Iron is necessary for the formation of protoplasm and cannot be replaced by other metals. Nitrogen, sulphur, phosphorus, carbon, hydrogen, oxygen, potassium, magnesium, and iron occur in the living cell. Chlorine is rarely, if ever, essential for plants. Aluminium is widely distributed in nature, but it is absent entirely, or almost entirely, from the majority of plants, although it does occur abundantly in a few species.

An enormous stream of water passes through plants, this water being in large part evaporated from the leaves; it contains salts which are retained by the plant. This rapid current of water is essential to the well-being of the plant, hence a large amount of salts is absorbed. These salts are absorbed by the cells selectively, and it is found that the proportions of mineral matter in plants are quite different from those of the outside world.

The mineral matters are not impurities but essential constituents of plants; they are derived from the soil in which the plant grows, and the composition of the soil determines to a large extent the ash of the plant. Thus, plants grown in a siliceous soil containing little lime were found to contain less lime in their ash than the same plants grown in a soil containing a large amount of calcium compounds. Further, a scarcity of potassium, magnesium, and iron was found in plants grown in soils containing much lime. In addition to the essential constituents of the ash, the plants also absorb non-essentials from the soils in greater or less quantity. For instance, sodium is found in the ash of all plants, but its duty has not yet been proved.

By drying and carefully burning we obtain the ash of plants and by analysis we ascertain its constituents, but we do not learn thereby the condition or combination in which the constituents existed in the plant. Calcium sulphate may exist in the ash produced by the union of the lime and the sulphur of the protein of the plant, but calcium sulphate did not exist in the plant itself. The

lime was probably present as oxalate or carbonate deposited in the substance of the cell walls or as carbonate on the surface of some leaves.

Ash always contains potassium, magnesium, calcium, and iron as nitrates, sulphates, chlorides, carbonates, or phosphates. The amounts of mineral matter vary for different parts of the plant, being very low in the woody tissues and very high in the leaves. In all cases the mineral matter is incorporated with organic matter. For instance, it is found deposited in the cell walls of plants. Silicon is absorbed as silicate by plants, and is found deposited in the epidermal cell walls. The grasses contain it in great abundance, but it rarely occurs in young organs. Organic compounds containing silicon have not been found in plants. Magnesium, besides existing in chlorophyll, is also found in the pectin of the cell membranes of plants, which has been found by F. Ehrlich (*Chem.-Zeit.*, 1917, **41**, 197) to be a calcium-magnesium salt of anhydro-arabino-galactose-methoxy-tetragalacturonic acid.

Besides the elements mentioned above, zinc, copper, manganese, bromine, and iodine are sometimes found in plants, generally in traces. These elements are drawn into the plant in solution from the soil, this solution being sometimes assisted by the carbon dioxide in the soil and sometimes by the sap exuded from the root hairs.

O. D. Roberts (*Analyst*, 1918, **43**, 254-259) found that part of the inorganic chlorine of the plant is sometimes lost during ignition, whilst the amount of sulphate is in excess of that originally present in the plant as sulphate. The inorganic constituents of the plant can only be obtained accurately by extracting the plant itself with water or dilute acids.

The mineral matter of cotton was given by Dr. Ure:

Potassium carbonate	44·80	per cent.
„ chloride	9·9	„
„ sulphate	9·3	„
Calcium phosphate	9·0	„
„ carbonate	10·6	„
Magnesium phosphate	8·4	„
Ferric oxide	3·0	„
Alumina and loss	5·0	„

Davis, Dreyfus, and Holland gave the following mean analysis:

Potassium carbonate	33·22 per cent.
„ chloride	10·21 „
„ sulphate	13·02 „
Sodium carbonate	3·35 „
Magnesium phosphate	8·73 „
„ carbonate	7·81 „
Calcium carbonate	20·26 „
Ferric oxide	3·40 „

According to Calvert (*Journ. Prakt. Chem.*, 1869, 122), the following amounts of phosphoric acid soluble in water are contained in the different cottons:

Egyptian	0·055 per cent.
New Orleans	0·049 „
Bengal	0·055 „
Surat	0·027 „
Carthagena	0·035-0·050 „
Cyprus	0·050 „

Barnes (*Journ. Soc. Chem. Ind.*, 1916, **35**, 1191), in discussing Indian cottons, found the ash varied from 1·18 to 3·71 per cent, and this was without any adulteration. The amount of the ash soluble in hydrochloric acid varied from 72·00 to 95·56 per cent, the remainder being taken as silica and silicates insoluble in boiling hydrochloric acid. The chlorine in the ash varied from 2·23 to 6·55 per cent. There was no connexion between the amount of mineral matter present in the ash and the moisture contents of the fibre, which fact seemed to indicate that these mineral substances had been taken up by the plant itself during growth, and were contained in the substance of the fibre. On burning the lint the skeleton nature of the ash assumed the original form of the fibre. The amount of the mineral matters contained in the ash will depend on the composition of the soil in which the plant is grown, and will (particularly the insoluble portion) have an effect on the

behaviour of the cotton during bleaching and dyeing. The composition of the ash was found to be :

	Bombay.	Punjaub.
Silica (mod. as HCl)	15·56	14·40
Alumina	10·80	12·87
Iron oxide	5·89	1·92
Lime	9·75	10·65
Magnesia	1·87	4·36
Sulphates (as SO_3)	1·96	2·52
Phosphorus pentoxide	3·26	4·46
Potash	27·32	26·03
Chlorine	6·55	3·84
Carbon dioxide	12·19	8·03
Soda	4·51	8·40
Undetermined and loss	0·34	2·52

Barnes states that it is impossible to remove the last traces of mineral matter from cotton by chemical treatment, and he concludes that this mineral matter is part of the fibre. The slightly acid pectins absorb some of the mineral matter, and then it is well known that cellulose has a high absorbent action on mineral salts in solution.

The occurrence of phosphorus in plants is discussed on p. 16.

Pectic Matters

Pectins occur in the intercellular spaces between the cells of fibres. They are complex bodies, being a mixture of several chemical individuals. As mentioned on p. 19, recent work on pectins has shown that the cementing substance, usually called pectose, contains a calcium-magnesium salt of a complex organic acid. Pectose exists along with cellulose in the substance of most cell walls. It has not been obtained pure in consequence of its close association with cellulose and the readiness with which it undergoes change in the process of extraction.[1] The reagents which separate it from cellulose convert it into pectin or into pectic acid, the former being soluble in water and the latter in alkalis. Pectose is also changed

[1] J. Reynolds Green, *Vegetable Physiology* (J. & A. Churchill).

by the action of natural ferments into pectin, which is the chief constituent of Irish moss. The ferment which causes this change is known as pectose.

Schweitzer's reagent dissolves out cellulose from the cell wall and leaves the framework, which contains pectose or a compound of copper and pectic acid.

Pectin swells up and dissolves in water, forming a viscous liquid which soon becomes a jelly. It is thrown down by basic acetate of lead. Boiled for some hours in water it is converted into parapectin, which is precipitated by neutral lead acetate; and further boiling with dilute acids converts it into metapectin, which is precipitated by barium chloride. Pectic acid does not dissolve in water, alcohol, or acids. It forms soluble salts with the alkalis, and insoluble ones with the metals of the alkaline earths. It dissolves in alkaline carbonates, phosphates, and in solutions of most organic ammoniacal salts, forming with them double salts which gelatinise with water. The solution in alkaline carbonates is mucilaginous, but when ammonium oxalate is the solvent it is perfectly limpid.

Metapectic acid is freely soluble in water and forms soluble salts with all bases, especially those of barium and calcium, which, however, precipitate pectic acid. Metapectic acid is the final product of the action of reagents on pectose; it does not form a jelly, its solutions being always limpid. It probably occurs in gums. With sulphuric acid one of the products is apparently arabinose.

Pectic bodies are found to be prominent in the layers of the cell wall remote from the protoplasm, and cellulose in those nearest to the interior of the cell. Pectic bodies are regarded by some chemists as compounds of carbohydrates of varied constitution with acid groups. Then cellulose is sometimes converted to lignin in the plant, this body being probably a mixture of substances formed successively from cellulose. It differs from cellulose in that it does not stain blue with iodine and sulphuric acid, but becomes red when treated with phloroglucinol and a mineral acid, and yellow with aniline chloride.

Barnes (*Journ. Soc. Chem. Ind.*, 1916, **35**, 1191), in discussing the pectins of cotton, refers to the work of

Mangin, showing that pectic matters consist of two classes of substances, viz., (*a*) neutral bodies resembling pectose, which is an insoluble compound closely resembling cellulose in its properties, and bodies of a gelatinous nature soluble in water, known as pectins; (*b*) faintly acid substances, the principal member of the group being pectic acid, which occurs in nature as calcium pectate. Such acids will account for the absorption of some of the mineral matter, and neutralisation of excessive acidity may be one of the functions of the alkaline salts in the sap of plants.

Colouring Matters

Many natural colouring matters exist in combination with proteins, *e.g.* indigo along with indigo gluten in the indigo plant, and it is for this reason that the colouring matters of raw textile fibres are fast. Magnesium chloride exists in cotton, and it also combines with proteins; like sodium chloride, it can be used to dissolve proteins, or at higher strengths to precipitate them from solution. Moreover, tannic acid also precipitates peptones (decomposition products of proteins), and tannic acid is found in fibres.

The chlorophylls are unstable, and are constantly undergoing reduction in the living cell. The replacement of chlorophyll by carotin is said to be the cause of the ruddy colour of autumn leaves. Some linen yarns are green (chlorophyll) and some are brown (carotin), and the same remarks apply to their benzene extracts. A greenish yarn after extraction by benzene becomes brown.

Schunck stated that cotton contains two colouring matters, one soluble in cold alcohol and the other in boiling alcohol. One contains 6·18 and the other 8·74 per cent of nitrogen. Marchlewski (*Journ. Chem. Soc.*, 1899, 84) obtained the colouring matter of cotton in crystals, which, he stated, had the composition $C_{13}H_{11}O_7$. He named this substance gossypol. It dissolves readily in alkalis to an intensely yellow-coloured solution, and also in sulphuric acid to give a characteristic crimson colour.

W. L. Balls states that about the 27th day of the development of the cotton plant a marked change takes place in the pigment layers, which has not been investi-

gated, but which is of considerable interest because it denotes the beginning of the second stage of boll maturation, during which the lint is given its strength. The change shows up in material which has been preserved in a mixture of acetic acid and alcohol. All the bolls from the first stage "pickle" to a green colour, which, of course, fades to a brown on exposure to light. From the 27th to the 45th day, however, the "pickle" thus made is at first pink and then bright red. The colour is probably connected with the development of pigment in the seed coat. When the boll is beginning to crack the "pickle" is brown.

The colouring matter of linen has been investigated by Bianchi and Malatesta (*Annali Chem. Appl.*, 1914, **1**, 281-291), who state that it consists of two definite acid colouring matters, one precipitated by basic lead acetate, and the other not precipitated by this solution. The reddish-yellow aqueous solution of the former, when treated with calcium hypochlorite solution, is partially bleached in a short time, and after some hours gives a yellow precipitate. The other colouring matter gives a clear yellow solution. On treatment with calcium hypochlorite the colour changes to pink after a short time, and after some hours is completely bleached. These observations are of interest in connection with experiments previously performed and described on p. 54. Bianchi and Malatesta also found that hemp contained two colouring matters, one precipitated by basic lead acetate and the other not.

Cellulose

The cell wall is formed from the protoplasm or secreted by it, and is usually known as cellulose: the thickening of the cell wall is a similar decomposition of the protoplasm. The plant produces from the carbon dioxide of the air, firstly, sugar, and subsequently starch and cellulose. The starch being in an insoluble form relieves the cell sap of its sugar, and thus enables it to go on making more sugar. Some of the carbohydrate is preserved by the plant as a reserve food, and is subsequently used by it; and some is used to form a considerable thickening of

the cell walls, and thus affords a permanent strengthening of the plant. This thickening is not always pure cellulose, but cellulose and pectic material may be present in varying proportions. The primary cell wall is a transparent membrane composed of cellulose; but associated with the cellulose are found other materials, such as pectoses, of which many forms have been described. Calcium pectate exists between the inner layers of the membrane. W. L. Balls states that the breaking strain of a fibre is very largely determined, if not entirely, by its weight, or, in other words, by the thickness of its cell wall; and there is good reason for believing that it depends on the sectional area of the walls, independent of their diameter.

The outer layers of the cell wall undergo a process of cuticularisation, which generally extends about half-way through its thickness. An apparently structureless membrane called the cuticle is produced, which prevents the absorption or dissipation of water or gases. It is made of *cutin* by this transformation of the cellulose or the pectose constituents. With iodine and sulphuric acid it is stained yellow, and turned brown by strong alkalis. Cellulose, when partially hydrated, turns blue with iodine; pectic bodies do not give any coloration.

J. König and E. Rump (*Chem.-Zeit.*, 1915, **39**, 257) found the difficultly soluble portions of vegetable cell membranes consist chiefly of three classes of substances, viz. pentosans, hexosans, and lignins. In each of these classes, one part, termed *proto*-pentosans, etc., is rendered soluble by enzymes or by water at 2-4 atmospheres pressure; a second and larger part, termed *hemi*-pentosans, etc., becomes soluble on boiling with 1-3 per cent acid at 2-4 atmospheres pressure; whilst a third still greater part, termed *ortho*-pentosans, etc., is only dissolved by strong acids or by dilute acids under higher pressure. The *ortho*-group, to which cutin and suberin also belong, can be further resolved by treatment with weak oxidising agents, when all lignins are oxidised and *ortho*-cellulose and cutin remain. Cutin and suberin are wax-like substances which cannot be oxidised or hydrolysed. They have similar carbon contents to the lignins (69-70 per cent), but contain more hydrogen (9-12 per cent). Lignins on oxidation give

carbonic, formic, and acetic acids. Microscopic evidence indicates that the substances accompanying cellulose are not chemically combined with the latter, but are structurally intimately mixed. Haas and Hill[1] state that lignocelluloses are considered by most chemists to consist of cellulose combined with at least two other non-cellulose constituents. One of these, A, appears to contain an aromatic nucleus, and the other, B, contains a furfural yielding complex, and is probably a pentosan. The two constituents, A and B, are sometimes grouped together as a single substance under the name of lignin or lignone. The constitution of this substance is still unknown. Suberin is said to consist of fatty substances, with glyceryl and other compound esters easily decomposed by potash.

There is no intention to give here an account of the properties of cellulose (because already many books give this), but to present a few items of interest to those engaged in the bleaching of fibres. Johnson and Hovey (*Journ. Soc. Chem. Ind.*, 1918, 136) discuss Cross and Bevan's claim that cellulose residues obtained from wood are not true celluloses of the same type as cotton cellulose, but that they are, in properties, true oxy-celluloses, giving furfural as a typical reaction, and state that the furfural reaction is by no means a characteristic reaction for any cellulose, since, for instance, the typical oxy-cellulose obtained by treating cotton with hypochlorites does not give this reaction. Moreover, these cellulose residues do not show the most typical oxy-cellulose reaction, namely, the high reducing power (copper number). M. Cunningham (*Chem. Soc. Trans.*, 1918, **113**, 173-181) states that the whole question of the structure of the celluloses remains open, and Cross and Bevan (*ibid.* 1918, **113**, 182-187) throw doubt on the usually accepted furfuroid pentosan relationship.

It is also evident that the celluloses should be re-grouped, or at least some definite distinction should be drawn between the groups suitable for plant physiologists and those suitable for chemists. With the advance in our knowledge of the constituents of fibres, these fibres ought now to be classed in groups according

[1] *The Chemistry of Plant Products* (Longmans, Green & Co., London).

to the nature of the cellulose which they yield on treatment. For instance, cotton and flax fibres contain similar non-cellulose constituents, although the proportions of these constituents are quite different. Further, the celluloses which are isolated from these fibres by the bleaching process are chemically indistinguishable, therefore these fibres ought to be classed in the same chemical group, in spite of the fact that one is a seed hair and the other a bast fibre. The use of such terms as pure-, pecto-, adipo-, etc., is not required to distinguish these fibres. It is true that flax contains a small quantity of woody matter, but this is of little importance in the chemical operations through which it is put, and the statement that flax cellulose is more easily hydrolysed than cotton cellulose is not supported by the observation of the author that 40 hours' boiling of linen yarn under pressure with alkalis had no apparent weakening effect.

If after isolating the cellulose from a fibre this cellulose is found to be different chemically from cotton cellulose, there is justification for putting it in another chemical group. Grouping in this manner will tend to simplify matters, and enable some order to be introduced into the present chaos of cellulose chemistry. In the case of another carbohydrate, viz. sugar existing in plants, sucrose is given that designation whether it be isolated from the sugar-cane, sugar-beet, or maple-tree. If, however, the sugar isolated is not identical with sucrose it is given another name. The same reasoning should apply to cellulose isolation, although, of course, the grouping is not such a simple matter as with sugars which can be separated by crystallisation. But take the case of the starches. It is known that all forms of starch occurring in the vegetable kingdom are not precisely the same (see A. R. Ling, *Annual Report on Progress in Applied Chemistry*, vol. ii., 1917), but it must be admitted that collecting these forms together and calling them *starch* has simplified matters and assisted progress in operations in which starch takes part. Recently it has been shown that the cellulose separated from straw is chemically indistinguishable from cotton cellulose.

The methods which have been used for isolating

cellulose from plant products, for the purpose of estimation, are of interest to bleachers. The principle of Cross and Bevan's method is (1) alkaline hydrolysis by dilute sodium hydroxide, then (2) exposure to chlorine gas, and (3) extraction with alcohol and ether. It is not the intention to discuss here this method, but in the light of conclusions given on p. 54 that chlorine does not bleach the colouring matter of linen, the use of hypochlorite solutions instead of chlorine gas might be preferable. Parker (*Journ. Phys. Chem.*, 1913, **17**, 219), in order to separate cellulose from cotton, treats the cotton with potassium hydroxide in a flask provided with a reflux condenser and standing in a paraffin bath heated to 130°-140° C. In this way cotton yielded 92·5 per cent of cellulose. This method can also be criticised from the information given regarding the elimination of the non-cellulose constituents of vegetable fibres during the bleaching process. The isolation of cellulose from any fibre can only be brought about after a study of the facts known to bleachers concerning the behaviour of that fibre during the different bleaching treatments. Again, it must be pointed out that bleaching is a matter of the economical isolation of cellulose on the large scale.

CHAPTER III

ELIMINATION OF THE NON-CELLULOSE CONSTITUENTS IN THE BLEACHING PROCESS

Object of bleaching—Drop in weight—Steeping—Drop in strength—Change in dimensions of cloth—Yellowing during storage.

As previously mentioned, the bleacher's duty is to remove the non-cellulose constituents of the fibre, that is, to separate the cellulose; and we will now consider the methods he uses to achieve this. These methods vary according to the material being treated and the purpose for which the bleached material is required, but the methods employed on the large scale differ mostly in details. For example, cotton cloth is steeped in water or dilute acid, in order to remove the materials added during the manufacture, washed, and then boiled in lime water or in a solution of caustic soda. After the lime boiling the cloth is washed well, steeped in dilute acids, washed well and boiled again, in this case with sodium carbonate solution; after the boiling with caustic soda the cloth is sufficiently "scoured" for many purposes and can be considered to be in a similar condition to the cloth given the lime and ash treatment, although, as will be explained later, there is a difference between the scouring actions in the two cases. The cloth is then steeped in a weak solution of a hypochlorite for some hours, washed, steeped in weak acid for some hours, and again washed. In this state the cloth is sufficiently bleached for some purposes, but for the production of white cotton goods it is usually given another boil with sodium carbonate solution, a wash, a further dip in hypochlorite solution, followed by a wash, a dip in weak acid, and a thorough washing. This is an

outline of the ordinary bleaching process, and we have now to consider how the various constituents of the raw fibre behave during these treatments.

J. C. Hebden (*Journ. Ind. Eng. Chem.*, 1914, 714-728) found on analysing samples of cotton from the caustic soda bleach that the following percentages of the original non-cellulose constituents were removed by the different operations.

	Steep.	1st boil.	2nd boil.	Chemic.	Sour.
Ash . . .	70·5	87·3	95·4	93·0	95·0
Protein (N × 6·25) .	...	91·5	91·7	92·2	92·7
Fat and waxes . (Ether extract)	5·5	20·4	64·0	67·8	69·6
Phosphoric acid .	60·0	100·0	...	...	

Bianchi and Malatesta (*Annali Chem. Appl.*, 1914, 1, 281-291) found the following particulars for raw and bleached flax.

	Ash.	Fat and Wax.	Aqueous Extract.
Raw .	·6-1·2	1·3-2	3-4 per cent.
Washed .	·6-·8	1·2-1·5	1-2 „
Bleached .	Rather less than washed		1-1·5 „
"Cream"	·4-·8	1-2	2 „

Cotton yarns decrease by about 6·5 per cent by weight during the bleaching process, but cotton cloth shows different figures, the drop being the sum of the non-cellulose constituents of the fibre and the matter added during the manufacture. The total drop is generally about 10 per cent of the original weight. The scouring operation causes the principal decrease in the weight, since most of the non-cellulose constituents of the fibre are removed during this operation. In some cases, after thorough scouring the cloth is almost white, showing that the colouring matter has been almost entirely removed, but in other cases the colouring matter resists removal by hot alkalis. The other constituents, however, are largely eliminated during the preliminary scouring. The following figures for the loss in weight of linen cloth during the bleaching process also show that during linen bleaching

the principal drop in weight takes place in the scouring. (S. H. Higgins, *Journ. Soc. Chem. Ind.*, 1911, **30**, 1295.)

	Weight gross.	Loss per cent.
Example 1.—Brown Linen . .	92·1	...
After steeping . .	88·7	3·8
„ lime boiling .	77·15	16·2
„ lye boiling . .	70·93	22·9
„ chemicing . .	69·53	24·5
Fully bleached . .	67·52	26·7

	Per cent.
Example 2.—Loss in lime boil . . .	9·6
3. „ „ lye boils . . .	15·9
4. „ „ „ „ . . .	15·15
5. „ „ "chemic" and sour . .	1·44

In Example 1 the scouring accounts for 86 per cent of the total drop in weight during the whole process, and therefore, for our purpose of finding out the way in which the non-cellulose constituents of the fibre are removed, the scouring operation is the one to be particularly studied. The decrease in weight is unavoidable if the scouring is done properly and the cloth is properly bleached. The figures show that so-called "half-bleaches" owe their weight entirely to the original non-cellulose constituents of the fibre being still retained by it.[1]

S. R. Trotman (*Journ. Soc. Chem. Ind.*, 1910, 249) showed that neutral salts, such as sodium chloride and sulphate, alumina, iron, zinc sulphate and calcium sulphate, had a large effect in hindering the scouring action of caustic soda, and it has been shown that starch has a similar effect. These observations point to the importance of washing the cloth well after a sour steep, that is, before going into the scouring kier, and also indicate the advantage of using pure chemicals. By means of steeping before scouring many of the impurities of the grey

[1] Knecht and Hall found for cotton yarn that the lime boil brought about a drop of 2·1 per cent in weight, and lime, sour, lye, about 4 per cent. Further treatment only brought about a small decrease in weight.

material, which are now known to affect the boiling process, are removed, and perhaps for the first time we have an explanation of the fact that the steep is found advantageous in so many cases. (Higgins, *Journ. Soc. Dyers and Col.*, 1912, **28**, 151-153.)

The disadvantage of allowing the cloth to cool in the kiers after the steam has been turned off is proved by Higgins (*loc. cit.*), since during the cooling some of the impurities removed by the hot lye are re-absorbed. E. Jentsch (*Färber Zeit.*, 1913, **24**, 29) also points to trouble after the lye boiling. Faults in dyeing were found to be due to not flooding the cloth with cold water when running off the lye after boiling; parts of the cloth touching the walls of the kier became overheated and developed oxy-cellulose. Also, by admitting caustic soda to the kier in too concentrated a state, faults resulted; slightly local mercerisation was said to be produced which resulted in dark stripes appearing in the goods after dyeing.

By the application of chemical reagents to yarns, considerable change in the structure of the yarn is observed; for example, the tensile strength is altered. This change must be discussed apart from the change in the cellulose of the yarn, which will be referred to later. O'Neill gives the following figures for the tensile strength of cotton threads before and after bleaching:

			Before bleaching.	After bleaching.
No. 1	Cloth.	Weft threads .	1714 grains	2785 grains
1	„	Warp „ .	3140 „	2020 „
2	„	Weft „ .	3407 „	3708 „
2	„	Warp „ .	3512 „	4025 „

showing that the bleaching process actually increased the strength of the thread. Huebner and Pope (*Journ. Soc. Chem. Ind.*, 1903, **32**, 70) showed that during the scouring the tensile strength of the cotton yarn was increased. It has previously been mentioned that on extracting the wax from cotton yarn the tensile strength is increased and, since the scouring removes a large proportion of the wax, it is probably for this reason that the strength is increased.

It is also noticed that on breaking single yarns they are liable to untwist and thus break sooner than they would do if their twist was preserved. After scouring they do not untwist so readily, the cohesion and consolidation being increased during the boiling. S. R. Trotman and S. J. Pentecost (*Journ. Soc. Chem. Ind.*, 1910, 4) found that the loss in length of yarn during the bleaching process was about 2·6 per cent, 5 per cent being allowed in commercial bleaching operations. For the count of the yarn, depending on the length and weight, they give the following changes :

Count before lye boiling.	Count after lye boiling.
24	25·70
32	33·72
40	42·0
70	72·58
80	83·90
100	104·60
120	125·60
150	167·50

F. P. Jecusco (*Journ. Soc. Dyers and Col.*, 1917, **33**, 34) found on boiling cotton with 3 per cent caustic soda and 2 per cent sulphated oil at 15 lbs. pressure for 8 hours there was a loss of weight of 6·45 per cent, a gain in strength of 22·8 and in elasticity of 0·95 per cent. With full bleaching the loss in weight was 7·3 per cent, the gain in strength 25·9, and in elasticity 0·79. The numbers vary with conditions, but in all cases the bleaching operation showed a substantial gain in strength and elasticity. If, however, the boiling process is restricted as to necessitate a more severe hypochlorite treatment, the total effect of the bleaching may result in a loss of strength. For example, on using soda ash in place of caustic soda for the boiling, and afterwards using a stronger hypochlorite solution, there was a loss of weight of 7·1 per cent and a loss in strength of 4·7 per cent.

Higgins (*Journ. Soc. Chem. Ind.*, 1911, **30**, 1295) found the following variations in tensile strength of linen yarns during the bleaching process :

	Tensile strength.
Example 1.—Brown yarn . . .	1270 grms.
After lime boiling . .	960 „
„ lye boiling . .	1070 „
„ chemic . . .	930 „
Fully bleached . .	910 „
Decrease in strength .	28·3 per cent.

Example 2.—Brown yarn . . .	950 grms.
After lime and lye boils .	730 „
„ chemic . . .	720 „
Fully bleached . .	710 „
Decrease in strength .	25·3 per cent.

	Warp.	Weft.
Example 3.—Brown yarn . . .	1050	800
After lime and lye boils .	890	860
„ chemic . . .	860	810
Fully bleached . .	780	740

The results show that lye boiling sometimes causes an increase in tensile strength, although, as shown by the figures on p. 31, the drop in weight in this operation is considerable. There is naturally a disturbance of the fibre by the removal of as much as 30 per cent of foreign matter from it, for in the case of cotton the decrease in weight is only about 5 per cent. After the effect of the scouring there is seen to be little further decrease in strength, thus showing that efficient bleaching removes the non-cellulose material from the neighbourhood of the fibre without appreciably impairing the tensile strength of the fibre itself.

The changes in dimensions, etc., of linen and cotton goods during the bleaching on the large scale is shown in the following table (Higgins, *Journ. Text. Inst.*, 1916, 29):

CREAM YARN GOODS. DAMASKS.

Piece No.	Brown Width inches.	Brown Length yards.	Brown Weight lbs.	Brown Weight dried out.	Moisture per cent.	Finished Width inches.	Finished Lengths yards.	Increase in Length yards.	Brown Width × Brown Length.	Finished Width × Finished Length.	Alteration in Area per cent.	Finished Weight.	Finished Weight, dried out.	Moisture per cent.	Drop in Weight, per cent.	Drop in Weight dried out, per cent.
1	71	42½	29¾	27½	7·6	68	43	½	3017·5	2924	−3·1	23½	21⅛	10·1	21	23·2
2	73	45¼	37	35 1/16	5·2	70	46½	1¼	3303·25	3255	−1·4	30¼	27 7/16	9·3	18·2	21·7
3	81	41	39	36 1/16	6·0	77	43¼	2¼	3321	3330	−1·3	32	28¾	7·15	18·0	21·6
4	71	41¾	32¼	30 7/16	5·6	68	42½	¾	2964·25	2890	−2·5	25 1/16	23¼	10·4	19·6	23·4
5	71	43¾	33½	31 7/16	6·1	68	45	1¼	3106·25	3060	−1·5	27 3/16	24½	10·0	18·8	21·9
6	71	39¼	29	27½	5·2	68	40¼	1	2786·75	2737	−1·8	23 1/16	21½	9·3	17·5	21·8
7	73	41½	33½	31 1/16	5·4	70	42¼	¾	3029·5	2957·5	−2·4	26 1/16	24½	8·2	20·4	22·9
8	73	41	34	32	6·0	70	42½	1½	2993	2975	− ·6	27 1/16	25	7·6	20·4	21·9
Average	...	...	...	...	5·9	...	...	1 5/32	...	...	−1·7	...	...	9·3	19·2	22·3

BROWN YARN GOODS. DAMASKS.

1	74	29	27½	26¼	4·5	70	30¼	1¼	2146	2117·5	−1·4	19 1/16	17¾	6·9	30·7	32·4
2	76	29¾	31	29	6·4	72	31	1¼	2261	2232	−1·3	22¾	20½	10·0	26·6	29·3
3	74	29	27½	26¼	4·5	71	30¾	1¾	2146	2183·2	+1·7	19 9/16	18	8·0	29	31·4
4	74	28¾	28½	27	5·3	71	30½	1¾	2127·5	2160·5	+1·6	20½	19	7·3	28·1	29·6
5	76	32	32½	30½	6·1	72	32½	½	2432	2340	−3·8	23¾	21¾	8·4	26·9	28·7
6	76	29¾	32½	30	8·3	72	30¾	1	2261	2214	−2·0	23 3/16	21½	8·2	28·7	29·2
7	74	30¼	31	29¼	5·6	70	31	1¼	2238·5	2170	−3·0	22⅝	20¾	7·3	27·8	29
8	74	29½	28	26½	5·4	71	30¼	¾	2183	2148	−1·6	20¼	18¾	7·4	27·7	29·2
9	74	29¾	27½	26	5·5	71	30¾	1	2201·5	2183·2	− ·8	19 9/16	18¼	6·7	29	29·8
Average	...	...	...	...	5·8	...	...	1	...	...	−1·7	...	...	7·8	28·3	30·0

COTTON GOODS. DAMASKS.

1	40	38¾	16½	15¾	4·5	38	39¼	½	1550	1491·5	−3·8	14 1/16	...	...	11	...
2	71	51½	32½	30 3/16	6·3	70	52	½	3656·5	3640	− ·4	29⅛	27½	8·0	8·3	8·9
3	58	52½	21⅛	20	5·3	56	51¾	−¾	3045	2898	−4·8	19¼	17⅞	8·3	7·7	10·6
Average	...	...	...	...	5·4	...	...	+1 1/32	...	...	−3·0	...	...	8·15	9·0	9·75

The yellowing of goods during storage has received much attention from chemists. Erban (*Färb. Zeit.*, 1912, 370) states that yellowing during steaming or storage is not due to the fats contained in the fibre, but to other constituents. Hebden (*loc. cit.*) regards the proteins as having more influence on this development than the fats. Levine (*Journ. Ind. Eng. Chem.*, 1916, 298), supported Hebden as regards the importance of the nitrogenous impurities, but also found that the ether-soluble impurities have an injurious effect, whereas the yellowing during steaming is not connected in any way with the presence of the alcohol-soluble impurities. R. E. Crowther (*Journ. Soc. Dyers and Col.*, 1913, 9), as opposed to Erban, regards proper scouring as the only way of preventing yellowing. He found that discoloration on steaming was not a function of the nitrogen contents of the cloth, and therefore was not due to chloramines. By treating brown cotton cloth with hypochlorites, washing, souring, and again washing, he found the cloth contained as little nitrogen as it did after lye boiling.

If the waxes of brown textile fibres are melted they become darker in colour, hence, if cloth containing wax be heated above the melting point of the wax, it becomes darker in colour. Experiments show (Higgins, *Journ. Soc. Chem. Ind.*, 1914, 902) that these waxes are only gradually removed during the bleaching process, and that the appearance and colour of the waxes are only slightly altered; hence on heating cloth at any stage of the bleaching process it will become darker in colour owing to the melting of the waxes contained in it. Good scouring, however, removes a large proportion of the non-cellulose constituents of the fibre, so that it is obvious that the more perfect the scouring the less chance there is of yellowing during storage. A sample of linen which had turned brown during steaming was found to be only a three-quarter bleach, *i.e.* it contained some of the original non-cellulose constituents of the fibre. Extraction with benzene and alcohol failed to remove the brown colour, and boiling with soda-ash solution only accentuated it, but boiling with soda ash, then chemicing and souring, that is, giving another turn of bleaching, removed the trouble.

Good scouring is the only method of preventing yellowing on storage (Higgins, *J. Soc. Dyers and Col.*, 1918, 35-53).

M. Freiberger (*Z. angew. Chem.*, 1916, **29**, 397) states that cloth bleached with cold hypochlorite solution and then soured did not keep so well as the same cloth bleached in a warm alkaline, and then in a warm acid bleaching bath. He later states (*Färber Zeit.*, 1917, **28**, 221-224, 235-236, 249-252) that the main cause of the yellowing of cotton is the presence of β-oxycellulose. Fats play no appreciable part in the yellowing of the goods during steaming, and fully scoured cotton is discoloured only slightly less than the raw goods. Chemiced goods show the strongest discoloration. Oxycellulose becomes quite brown on steaming, about 100 times darker than cellulose. B. Haas (*Papierfabr.*, 1914, **12**, 891) had previously stated that fabrics bleached with bleaching-powder solution showed the greatest tendency to discoloration, those bleached with electrolytic liquor were better, and those bleached with sodium peroxide were almost stable in colour. In the case of the bleaching-powder solution the trouble is said to be due to the fixation of alkaline earth compounds on the fibre. Moreover, the benefit of soft water in the bleaching process is lost. If fabrics heat up on leaving damp in a heap, the temperature produced depends on the state of purity of the fabrics, and the nearer the cellulose approaches a state of complete purity the more stable is the bleached colour. Higgins[1] mentions an American works which bleached cotton cloth by "wetting out," saturating with bleaching-powder solution and allowing to lie, washing in a machine, souring, and again washing. These goods were found to deteriorate in stock, because the non-cellulose constituents of the cloth had not been removed but merely oxidised and left in the fibre to cause trouble afterwards.

Higgins (*Journ. Soc. Chem. Ind.*, 1914, 702) found a loss in weight of 9 per cent and of strength of 16 per cent in "creaming" linen yarn. The loss in weight was made up of 1·01 per cent due to the acid treatment; 2·03 per cent due to washing with water; and 5·96 per cent due to oxidation by the hypochlorite.

[1] *The Dyeing Industry* (Manchester University Press).

CHAPTER IV

ELIMINATION OF THE WAXES OF FIBRES DURING THE BLEACHING PROCESS

Effect of lime boil—Caustic soda boiling—Volatile solvents and waxes—Hypochlorites and waxes—Reducing properties of waxes—Boiling with baryta and strontia.

After the caustic soda bleaching process the figures of Hebden show that 30 per cent of the original fats and waxes remain after the full bleaching. Knecht (*loc. cit.*) states that the waxes are not entirely removed by bleaching cotton. In the case of linen cloth, Higgins (*loc. cit.*) found that the waxes were gradually but not entirely eliminated during the bleaching:

	Wax per cent.
Original linen . . .	1·47
After water boiling . . .	1·42
„ lime boiling and souring .	1·59
„ 1st lye boil . . .	0·25
„ 2nd lye boil . . .	0·11
„ 1st chemic . . .	0·11
Fully bleached . . .	0·036

The percentage of wax was calculated on the original weight of the brown linen in all cases. Other pieces of bleached linen were found to contain from 0·02 to 0·045 per cent of wax. In the lime boil the waxes are saponified but not removed; the unsaponifiable portion remains attached to the fibre, and also the lime soap produced by the union of the fatty acids liberated during

the saponification, and the lime. By considering the composition of the wax of linen (p. 13), it is seen that solid alcohols are liberated by the hydrolysis, and these are also soluble in the benzene used for the extraction.[1] It is for this reason that the extract after the lime boiling and souring was greater than from the original linen. A large number of experiments were carried out to determine this increase in weight; in one case the extract increased from 1·65 to 1·88 per cent. Also it must be remembered (as pointed out on p. 12), that on souring linen and cotton before extraction, the percentage of extract is increased; in the last example mentioned, this previous souring brought the wax extract of the original yarn to 1·81, thus only leaving 0·07 per cent to be accounted for by the solid alcohols produced during the saponification, and soluble in benzene.

The wax extracted from linen after lime boiling and souring was found to contain 40 per cent saponifiable matter, whereas the wax extracted by benzene from brown linen only contained 27·8 per cent saponifiable. This difference was due to the amount of wax which is extracted from linen after souring, subsequent to the benzene extraction (p. 12). A large number of tests showed this. Similar results were obtained in the case of cotton.

Hanks of linen yarn were given the treatments mentioned in the following table, and their wax contents then determined :

	Decrease in Weight per cent.	Wax per cent.
1. Lime, lye, lye .	21·8	0·06
2. Lye, lime, lye .	...	0·046
3. Lye, lye, lye . .	...	0·16

Sample No. 3 was by far the dullest in appearance, and the figures show that it contained by far the most wax.

The lime boil has long been a topic of arguments between chemists and bleachers. The former state that caustic soda is the best saponifying agent, and the latter reply that the lime boil cannot be replaced for certain

[1] All fats contain a small quantity of the monohydric alcohols, cholesterol and phytosterol, which form what is known as the unsaponifiable residue of fats.

classes of goods. Lime boiling is not a mere survival of the days of empiricism; it is the best treatment for some classes of goods, for the figures given above show that it is the best means of removing the waxes from the fibre. After the lime boil and sour we have on the fibre the unsaponifiable portion of the wax and free fatty acids, and when the contact with alkali takes place in the lye boil, a soap is readily produced with the free fatty acid, and the rapid emulsification and elimination of the unsaponifiable portion results. Shorter found that on adding a solution of an alkali to a mixture of a mineral oil and a fatty acid, the emulsification was practically spontaneous, and he explained this as being due to (1) the rapidity of the formation of the soap layer; and (2) the plasticity of the layer. We have these conditions produced in the case of the lime boiled and soured cloth being led into the soda ash lye, for the wax of the cloth here consists of a fatty acid and an unsaponifiable substance like mineral oil (Higgins, *Journ. Text. Inst.*, 1916, **7**, 30). S. A. Shorter (*Journ. Soc. Dyers and Col.*, 1918, **34**, 137) states the emulsifying effect of alkalis is an interesting example of surface reaction. An alkaline solution will emulsify an oil only when the latter contains a sufficient amount of free fatty acid. The effect is due to the formation on the surface of a layer of soap, which modifies the properties of the layer in such a way as to facilitate the splitting of the oil into small drops. If there is not sufficient fatty acid to form a soap solution of the necessary strength, alkali alone will not act as an efficient detergent, and it is necessary to use soap. He states[1] that the above explanation of the efficacy of the lime boil is convincing. In this connection it is interesting to note that Scheurer and Wallach (*Bull. Soc. Ind. Mulhouse*, 1913, **83**, 510) find mineral oil if mixed with vegetable oil to at least 60 per cent becomes emulsified on boiling with alkalis.

The extraction of linen yarns and fabrics with volatile solvents before scouring has been protected (J. Burt Marshall, Ltd., and S. H. Higgins, Eng. Pat. 102892 of 1916) in order to dispense with the boiling with lime,

[1] Private communication.

caustic soda being used instead. J. F. Briggs (*Annual Reports on Progress in Applied Chemistry*, 1917) makes the following remarks on this process: "S. H. Higgins, following up his previous study of the chemistry of flax wax (*loc. cit.*), in which it was shown that the wax of linen fabrics could not be advantageously attacked by boiling with soda alone, has regarded the presence of this wax as the chief *raison d'être* of the tedious preliminary lime boil and 'black sour,' and claims that this treatment, with its attendant danger of lime stains, may be avoided by a preliminary extraction of the goods with volatile solvents, after which the soda boil may be applied direct. The flax wax thus obtained is a complex mixture, from which the true hard wax may be separated by suitable purification. In times like the present the wax by-product possesses very considerable value, but it remains to be seen whether the treatment proposed is technically and economically justified."

Returning to the effect of the lime boil we find chemists are by no means agreed that this treatment has any advantage over the caustic soda treatment. For instance, Trotman and Thorp[1] give the following comparisons of goods bleached by the two methods:

	Experiment 1.		Experiment 2.		Experiment 3.	
	Soda boil.	Lime boil.	Soda boil.	Lime boil.	Soda boil.	Lime boil.
Ash	0·26	0·52	0·26	0·50	0·42	0·56
Free fat . . .	0·10	0·26	0·20	0·15	0·16	0·11
Fatty acids (as soap) .	0·16	0·22	0·13	0·21	0·26	0·56
Nitrogen . . .	0·05	0·07	...	...	0·07	0·07

The following figures (C. Beadle and H. P. Stevens, *Journ. Soc. Chem. Ind.*, 1913, **32**, 174) show the effect of removing the wax from cotton on its power of taking up water. Samples of cotton of the various kinds mentioned were dropped on to water, and the times they required to become immersed were measured.

[1] *Bleaching and Finishing of Cotton Goods* (C. Griffin, Lond., 1911).

		Mean of 4 Tests.
Cotton wool (ordinary) . . .	more than	24 hrs.
Cotton bleached, but not scoured . .		31·3 secs.
Cotton boiled in 1 per cent NaOH . .		12·3 „
Cotton boiled in 2 per cent NaOH . .		5·7 „
Cotton boiled and bleached and boiled again		4·0 „
Cotton after extraction with ether and alcohol		·5 „

The maximum effect of the caustic soda was produced by three hours' boiling.

Various methods have been proposed for more effectively removing the waxes during the scouring operation. Peckham (*Met. and Chem. Eng.*, 1916, **4**, 160) boils the cloth in a soap solution containing benzol, and S. Dyson (Eng. Pat. 10311 of 1913) uses a solution containing potash soap, carbon disulphide, and olein for removing grease from fabrics. Resin soap, along with the alkali, has long been used, apparently with the same reason; but tests of the efficacy of the substance are difficult, because some of the resin invariably adheres to the cloth after the treatment, and is dissolved out by solvents during the experiments. Benzol and other solvents brought into an emulsion with Turkey red oil and water have also been used. These preparations act in an efficient manner, but their cost does not admit of their extensive adoption on the large scale.

The *effect of hypochlorites on the waxes* was investigated by Higgins (*loc. cit.*). "Cream" linen yarn was found to contain 1·21 per cent of wax, which was apparently little different from the original wax. On saponification, however, it was found to contain 60 per cent of saponifiable matter. The chemicing process, therefore, changes the wax into products which yield to a larger extent to saponification, thus explaining the observation that chemicing prepares the impurities for removal by the scald. Cotton cloth gave similar results. During the saponification a white solid was produced, and was apparently potassium chloride formed by the union of the chlorine of the chlorinated wax with the potash of the alcoholic potash used for the saponification.

Knecht (*loc. cit.*) has referred to the reducing effect of some of the constituents of the cotton fibre, and Hofmeister has mentioned bodies of an aldehydic nature in flax wax. These reducing agents cause the bleeding of vat colours in the lye boil, and to prevent this action J. Graf (Ger. Pat. 288751 of 1914) pads the cloth with caustic soda, to which non-oxidisable salts have been added. The goods are allowed to lie for some time before boiling. L. Kollmann (*Papierfabr.*, 1910, **8**, 863-869, 890-893) gives the following figures to show the changes in the reducing power of a given sample of raw cotton in the course of the usual bleaching process. The results show milligrammes of permanganate reduced by 100 grammes of cotton in one hour:

Raw cotton	569
After lime boil	402
After ash boil	223
After bleach	171

The greatest reduction in the power is shown after the lye boil, when the waxes and proteins are largely eliminated. R. Scholl (*Ber.*, 1911, **44**, 1312) states that the reducing properties of cellulose, which are shown in its behaviour towards Fehling's solution, may also be shown by certain vat dye-stuffs. A flavanthrene vat may be prepared by means of overbleached cellulose, by boiling the latter for half-a-minute with 2N-sodium hydroxide and a little of the dye-stuff. W. F. A. Ermen (*Journ. Soc. Dyers and Col.*, 1912, **28**, 132) describes an improvement of Scholl's test for oxycellulose given above.

For the effect of enzymes on waxes see p. 116.

The use of baryta and strontia in place of lime for boiling cotton goods has often been tested. R. Weiss states (*Bull. Soc. Ind. Mulhouse*, 1914, **87**, 420-506) that baryta is inferior to lime for this purpose, but strontia has a much more rapid saponifying action. It is, however, more costly and tends to cause damage.

CHAPTER V

ELIMINATION OF THE PROTEINS IN THE BLEACHING PROCESS

Drop in nitrogen during bleaching—Non-protein nitrogen—Chloramines of no importance during bleaching.

During the hydrolysis of natural proteins carbon dioxide and ammonia are formed in varying amounts. The production of calcium carbonate during lime boiling and of sodium carbonate during caustic-soda boiling is due to the evolution of carbon dioxide, and the liberation of ammonia accounts for the peculiar smell of the kier house of bleachworks. When proteins are boiled with alkalis some of their sulphur is split off as alkali sulphide. The amount of this is between one-third and two-thirds of the sulphur of the protein. Since, as shown later, efficient scouring effectively removes the proteins from textile fibres, it can therefore be said that the sulphur is also removed during this operation.

The nitrogen of Egyptian cotton was found by Schindler (*Journ. Soc. Dyers and Col.*, 1908, **24**, 106) to vary from 0·250 to 0·256 per cent. On boiling with caustic soda of 2° Tw. these quantities were reduced to 0·064 and 0·066 per cent; caustic soda of 10° Tw. brought the nitrogen down to 0·028, and of 77° Tw. to 0·019 and 0·016 respectively. Thus on boiling with caustic soda the bulk of the nitrogen of the cloth goes into solution in the caustic liquor. Ammonia, corresponding to 0·06 per cent of nitrogen, was evolved during the boiling with the strongest solution of caustic soda. Trotman found 0·05 per cent of nitrogen in cotton after the caustic boil, and

Hebden (*loc. cit.*) found 91·5 per cent of the nitrogen was removed by steeping and boiling cotton cloth with caustic soda.

From a consideration of the methods used for separating proteins (p. 17), it is seen that the bleacher, by using water, dilute acids, and hot dilute alkalis, employs the best reagents for this separation, therefore it is to be expected that a large proportion of the protein of the fibre will be removed. Proteins are hydrolysed when boiled with caustic soda or lime; and although the separation of these products of hydrolysis is difficult, the estimation of the ammonia given off during the hydrolysis is an easy matter, and gives some clue as to the nature of the products of hydrolysis. It is usual in determining the protein of vegetable products to determine the nitrogen and then multiply by 6·25, but this method is not satisfactory, since some vegetable products only contain half their nitrogen as protein. Higgins (*Journ. Soc. Dyers and Col.*, 1919) used the method of Osborne, Leavenworth, and Brautlecht (*Amer. J. Physiol.*, 1908, **23**, 180-200) for detecting and approximately estimating proteins. In this method the protein is distilled with caustic soda, the flask being replenished by water and distilled until no more ammonia is evolved. In the case of linen yarn it was found that the whole of the nitrogen was given off during three distillations, whereas cotton required as many as eight distillations to drive off all the ammonia. These observations are discussed in the light of the results obtained by Osborne when distilling other proteins.

Using this distillation method of approximately estimating proteins, cotton cloth was found to lose a large amount of its protein (used in sizing the warp yarns) by steeping and washing, and unsized cotton yarn was found to give up about one-third of its protein by steeping in neutral salt (sodium chloride) solution. Distillation with lime showed that the lime effectively hydrolysed the protein, but the products of the hydrolysis being only partly soluble were not completely removed from the cloth as in the case of caustic-soda boiling. Steeping in dilute acid was also found to remove some of the protein from cotton yarn.

Cotton yarn boiled with caustic soda under low pressure on the large scale was found after well washing to give off no appreciable amount of ammonia on distilling with caustic soda as above described, therefore it was concluded that the caustic-soda boil effectively removed the proteins from the fibre. It was found that boiling with soda ash had also the same effect. After lime boiling and souring the yarn yielded an appreciable quantity of ammonia on distillation; a second lime boil and sour reduced this amount, but still the ammonia evolved was appreciable. As previously mentioned, this observation was not due to incomplete hydrolysis, but to the products of the hydrolysis clinging to the fibre. A soda-ash boil after the lime boil and sour, that is, the complete scouring usually given after the lime boil, was found to remove all the protein. Hebden (*loc. cit.*) found that the first lye boil removed 91·5 per cent of the nitrogen, and a second lye boil 91·7 per cent—that is, on washing the cloth well after the first lye boil, and then boiling in freshly made alkali, only a further 0·2 per cent of nitrogen was eliminated, leaving 8·3 per cent still present on the fibre. Obviously this nitrogen cannot be present as protein, but as some other nitrogen compound. That this residual nitrogen is not protein nitrogen is supported by Hebden's figures showing the elimination of phosphorus during the bleaching. Phosphorus occurs in the protein of the nucleus of plant cells, and as 60 per cent of the phosphorus was removed in the steep, and 100 per cent at the end of the first lye boil, it follows that the protein containing the phosphorus was all removed by the lye boil.

The results obtained in the case of linen yarn showed that caustic soda again effectively removed the proteins of the fibre as also did the scouring process—lime boil, sour, and lye boil. In the case of soda-ash boiling, however, it was found that the proteins were not all removed from linen. Lime boiling gave results similar to those obtained with cotton. Commercial "cream" and "boiler" yarns were found to contain a large amount of protein.

Proteins have been found to react with chlorine

yielding chloramines, which bodies have lately become important as antiseptics for wound treatment. The chloramines are relatively stable, and the chlorine they contain is "active" in the sense of the activity of hypochlorite chlorine. C. F. Cross, E. J. Bevan, and J. F. Briggs (*Journ. Soc. Chem. Ind.*, 1908, **27**, 260) state that chloramines are conspicuous in flax bleaches, that they are relatively stable and resist washing, and are present in yarns and cloth, fully washed from the ordinary bleaching operation, and if dried, even after further souring followed by exhaustive washing, they persist, and are only slowly decomposed on storage. Decomposition is attended by the production of acid, and hence the particular cause of damage to textiles, frequently observed but previously unexplained. R. E. Crowther (*Journ. Soc. Dyers and Col.*, 1913, **29**, 38), experimenting with cotton, found that hypochlorites were very difficult to wash out of cotton goods, but if the washing was continued up to twelve hours the whole of the chlorine was removed. Cotton yarn after chemicing and washing was spotted with ultramarine and heated in a stove for four hours. The ultramarine was not affected, therefore no acid was liberated during the heating; hence he concluded that chloramines were not present in the cloth before heating. Other experiments led him to the conclusion that chloramines were not produced on cotton.

It is shown above (Higgins, *loc. cit.*) that cotton and linen, when scoured with (*a*) caustic soda or (*b*) lime, sour, soda ash, are incapable of forming chloramines on treatment with bleaching-powder solution because they no longer contain proteins. Now this treatment is the minimum to which cotton and linen goods are exposed in large scale operations before the goods are treated with hypochlorite, therefore one can safely conclude that the existence of chloramines is of no interest to the bleacher of cotton and linen goods. Cotton boiled with soda-ash is also found to lose practically all its protein, but in the case of linen the result is quite different, since tests showed that eight hours' boiling in soda-ash solution did not serve to remove all the protein from linen yarn, and also that commercial "boiled" linen yarns contained a

large amount of protein. When commercial "boiled" yarns are brought into contact with hypochlorite solution, then washed, soured, and washed, to produce commercial "cream" yarns, we have here the only instance of the possibility of the existence of chloramines in the bleacher's experience. The protein of the fibre, which resists the action of the soda-ash solution during the boiling, is unchanged by the treatment because boiling alkaline carbonates do not coagulate proteins, but merely remove them, therefore the "boiled" yarn going into the hypochlorite to produce the "cream" yarn contains a portion of the proteins of the original fibre. On distilling the "cream" yarn with caustic soda in the way previously described, it was found to give off ammonia in precisely the same manner as the original linen yarn did, and, moreover, the evolution of ammonia also suddenly ceased with the third distillation. A detailed examination of the cream yarn will be given later.

The nitrogen contents of cotton piece goods containing flour sizing are higher than linen goods, which are never sized with materials having a high nitrogen content, and since during boiling these nitrogenous bodies become soluble, the statement of Cross, Bevan, and Briggs (*loc. cit.*) that "cotton cellulose is permanently stained by taking up the products (containing nitrogen) of the action of alkalis on the flax constituents" is difficult to reconcile. Moreover, their statement that "the nitrogen constituents of fibres are extremely resistant, and are only gradually broken down by alkaline boils, is not borne out by the experiments described above."

From experiments on the washing of "cream" yarn goods and on the retention of chlorine by cotton and linen, Higgins (*Journ. Soc. Dyers and Col.*, 1918, 35-43) concluded that the deterioration of imperfectly bleached textile fabrics during storage was due to mineral acids which had not been thoroughly washed out of the goods; that the chlorine reaction of chemiced and washed cloth was due to free chlorine; and that there was no evidence that chloramines play any part in the deterioration. Experiments performed to eliminate the nitrogen from cotton and linen showed that this elimination had no

effect on the retention of "active" chlorine by the fibres, thus showing that this chlorine did not exist as a nitrogen compound in the fibre. The method suggested by Cross, Bevan, and Briggs (*loc. cit.*) to destroy hypochlorites and leave chloramines unaffected, by adding hydrogen peroxide was not found to destroy free chlorine, to which the reaction of the fibres with potassium iodide was due. Iodine is absorbed by textile fibres in a somewhat similar manner to dye-stuffs, and it was shown (Higgins, *Journ. Soc. Chem. Ind.*, 1909, **28**, 188) that unbleached, bleached, and mercerised cotton absorb different quantities of iodine from a potassium iodine solution of iodine, these quantities being in the same proportion as the amounts of substantive cotton dye-stuffs which the different forms of cotton absorb from aqueous solutions of these dye-stuffs. Moreover, the washing out of the iodine and of dye-stuffs from the fibres were found to be similar processes. It has never been contended that substantive cotton dye-stuffs form chemical compounds with the cotton fibre, and this contention cannot be made in the case of iodine and textile fibres. Similarly, the retention of chlorine by the fibres is not a function of the nitrogen contents of the fibre. Using permanganate as the bleaching agent instead of hypochlorite, and thus avoiding the production of chloramines, it was found that the cloth thus bleached became "tender" on stoving owing to the presence of acid which was extremely difficult to wash out of the cloth. In order to avoid the trouble of acid "tendering," which was proved to be the cause of deterioration during storage or stoving, the use of soluble hypochlorites, *e.g.* sodium hypochlorite, and the omission of the acid treatment was suggested by Higgins for the production of "cream" linen yarns.

A further discussion of this subject is given in letters by C. F. Cross, S. H. Higgins, and J. F. Briggs in the *Journ. Soc. Dyers and Col.*, 1918, but it is interesting to note a previous controversy on this matter. C. G. Schwalbe (*Z. angew. Chem.*, 1908, **21**, 302-303) controverted the statement of Cross and Bevan that during the bleaching of wood pulp chlorine combines with the residual non-cellulose constituents of the pulp forming organic chlorinated

compounds, some of which are volatile, whilst others may remain fixed in the fibres after washing. Using both bleaching-powder solution and sodium hypochlorite Schwalbe found that there was a very small quantity of chlorine both in the organic volatile form and in the ash. He concludes that no appreciable chlorination of the pulp takes place, and that the products of the bleaching are removed during the process of washing.

E. Knecht and W. Hall (*Journ. Soc. Dyers and Col.*, 1918, 220) found that cotton after the scouring and first chemic had lost 91·3 per cent of the nitrogen which it originally contained. Since many cotton goods are further soured, washed, boiled with soda ash, chemiced, soured, and washed, the elimination of the nitrogen must be very nearly 100 per cent by this time. The same remarks also apply to the linen bleaching process.

In connection with the proteins above mentioned the following claim by C. Bennert (Ger. Pat. 304003, 1915) is of interest. Crude solutions containing protalbic and lysalbic acids or their salts, such as are obtained by the hydrolysis of proteins by caustic alkalis, are treated with magnesium hydroxide to give protein derivatives which are useful as detergents and are also employed in the textile industry, particularly in dyeing and printing. They are purified from other compounds which give insoluble compounds with lime and magnesium salts.

CHAPTER VI

ELIMINATION OF THE MINERAL AND PECTIC MATTERS DURING THE BLEACHING PROCESS

Mineral matter removed at different stages—Potash in caustic lye—Pectins and acids.

BARNES (*loc. cit.*) states that the amount of ash in bleached cotton varies from 0·1 to 0·6 per cent, while special filter paper, prepared for laboratory use by treatment with hydrochloric and hydrofluoric acids, still often contains as much as 0·03 to 0·05 per cent of ash. As far as we at present know it is impossible to remove the last traces of ash by chemical treatment.

A consideration of the nature of the mineral constituents will indicate that the treatment of the fibres, at different stages of the bleaching, with acids will eliminate some of the mineral matter, and experiment shows this to be the case. Thus Knecht found that the acid extract of cotton contained a large amount of mineral matter, and the extraction of magnesium from the fibre by means of hydrochloric acid is mentioned on p. 12. Hebden's figures show that only 5 per cent of the original ash remained in the cloth after the caustic soda bleach. Higgins found in the case of linen cloth that as the non-cellulose constituents of the linen were removed the ash decreased in about the same ratio; there was no great decrease in weight after the scouring and also the ash contents of the linen remained almost constant.

	Ash per cent.
Brown linen cloth . . .	1·28
After lime boil and sour . .	0·18
„ lye boils . . .	0·084
„ chemic and sour . .	0·08
Fully bleached . . .	0·074

Half-bleached linen, which was of a grey colour and contained some of the original non-cellulose constituents of the fibre, was found to give 0·37 per cent of ash.

E. Knecht and W. Hall (*Journ. Soc. Dyers and Col.*, 1918, 220) found that the alcohol extract of cotton yarn contained about 40 per cent of ash, of which about 20 per cent was potassium. The water extract contained about 50 per cent of mineral matter, about 20 per cent being potassium. Both extracts were faintly acid to litmus. The potassium in both extracts was 0·376 and 0·480 per cent of the weight of the yarn for American and Egyptian yarn respectively. The formic acid and hydrochloric acid extracts were also mainly mineral. The mineral matter in the yarn consisted of K_2O, Na_2O, MgO, and Al_2O_3 (with a trace of iron in the American yarn), and CO_2, Cl, P_2O_5, and SiO_2 (traces).

The ash contents were :

	Before extracting.	After extracting.
American .	0·931%	0·076%
Egyptian .	0·17%	0·076%

After the lime boil, sour, lye, sour, chemic and sour the ash contents were reduced from 0·89 to 0·15 per cent, the ash remaining on the fibre being principally silica.

The pectic matter is practically all removed during the scouring, but before it is all removed it is probable that the material must be soured because of the calcium and magnesium united to the pectic matter (p. 21). Knecht and Hall concentrated the liquor obtained by boiling cotton yarn with lime water and then added alcohol. A precipitate was obtained which was apparently pectic acid, so that the pectic matters are removed to some extent in the lime boil. The subsequent lye boil removes a further amount.

B. Leech (Eng. Pat. 104202 of 1916) removes pectic matter from cotton by means of aqueous hydrochloric acid at or near its boiling-point. The pectic matter is removed as pectic acid, and soluble chlorides are also eliminated. The conditions are chosen so as to prevent a serious loss of strength of the fibre.

CHAPTER VII

DESTRUCTION OF THE COLOURING MATTER BY OXIDISING AGENTS

Bleaching action of hypochlorites—Chlorine water a bad bleaching agent—Metallic oxides and hypochlorites—Effect of neutral salts—Effect of chlorides—Hypochlorous acid as a bleaching agent—Properties of hypochlorite solutions—Old chemics—Bleaching agents and antiseptics—Drying of bleaching powder.

This subject might be called bleaching itself, but it must be remembered that the operations, previous to the treatment of the material with decolourising solutions, remove a large amount of the colouring matter from vegetable yarns and fabrics. Sometimes cotton cloth after thorough scouring is only slightly coloured, there being little work for the decolourising solutions to perform; but in the case of goods made from Egyptian cotton the material is generally dark in colour in going into the chemic. A large amount of the colouring matter of linen is removed before the linen enters the chemic, and properly scoured cloth uses up much less chemic than cloth imperfectly scoured (see p. 120). The colouring matter with which the bleacher is concerned is the small amount which remains after the full scouring process. This colouring matter has resisted long boiling with alkalis and treatment with dilute acid, so other means are adopted of getting rid of it. Treatment with solutions of hypochlorites is the method adopted in nearly all cases, and the hypochlorite of lime, viz. bleaching-powder solution, is generally used, although sodium hypochlorite is also used.

Text-books of chemistry state that the bleaching action of bleaching-powder solution is due to the presence of calcium hypochlorite, which, with hydrochloric acid, yields chlorine; and it is sometimes understood that the process

of bleaching consists of dipping the cloth into bleaching-powder solution and then into acid. Actually, however, the goods are bleached by immersing them in bleaching-powder solution until their colour is practically destroyed, then washing well, dipping into acid and again washing. The use of acid is not essential, and it is principally employed to remove basic calcium compounds from the cloth; when sodium hypochlorite is used in place of bleaching-powder solution the treatment with acid is often omitted. The bleaching action of hypochlorite solutions must therefore be explained without reference to the subsequent immersion in acids. Davy did not consider the bleaching action of hypochlorites to be due to their generation of chlorine, for he states (*Phil. Trans.*, 1811, **101**, 1-3, 12-35), "The hyper-oxymuriates seem to owe their bleaching power entirely to their loosely combined oxygen; there is a strong tendency in the metal of those in common use to form simple combinations with oxymuriatic gas, and the oxygen is easily expelled or attracted from them."

R. L. Taylor (*Chem. Soc. Trans.*, 1910, **97**, 2541) stated, "It is usually understood that a pure solution of hypochlorous acid bleaches more energetically and more rapidly than free chlorine. I have prepared practically pure solutions of hypochlorous acid and compared its action with chlorine on various colouring matters, and I have failed to find any evidence of the greater activity of hypochlorous acid. I am strongly of the opinion that, in practice, hypochlorous acid plays only a minor part in bleaching. The active bleaching agent is probably free chlorine." As this statement was against experience in the bleaching industry it was attacked by Higgins (*Chem. Soc. Trans.*, 1912, **101**, 222), who showed that free chlorine had practically no action on the colouring matter of linen. Taylor (*Journ. Soc. Dyers and Col.*, 1912, **28**, 151-153) admitted this fact in the following words: "This peculiarity of linen with respect to the action of chlorine was first pointed out by S. H. Higgins (*Journ. Chem. Soc.*, 1912, 222)," and he further stated that the activity of bleaching liquors upon natural colouring matters cannot be measured by their activity towards simple dye-stuffs such as turkey-red and indigo. The

latter statement is of course obvious, for the action of chlorine on artificial dye-stuffs has to be considered in the light of the chemical constitutions of these dye-stuffs. Thus, some substantive cotton dye-stuffs are immediately destroyed by chlorine or hypochlorites, whereas others are apparently unaffected. We are now concerned with the bleaching of the natural colouring matters of textile fibres such as is carried out in industrial bleaching.

Higgins showed (*Journ. Soc. Dyers and Col.*, 1912, **28**, 30) that the evolution of oxygen from bleaching-powder solution in contact with copper oxide and from a solution of sodium peroxide in contact with the same oxide were similar actions; and, further, that they were similar to the action of bleaching-powder solution on the colouring matters of textile fibres. In short, the actions were in all cases a direct production of oxygen. He also showed that on acting on linen cloth with very dilute solutions of bleaching powder the action was a unimolecular one:

$$\frac{1}{t} \log \frac{a}{x} = \mathrm{K},$$

K being approximately a constant (*Chem. Soc. Trans.*, 1913, **103**, 1816), and therefore the hypochlorite bleached by giving up its oxygen directly to produce the oxidation of the colouring matter. This conclusion was confirmed by observing the action of dilute hypochlorite solutions on cotton cloth dyed with indigo, the action being again found to be unimolecular.

Taylor now stated (*Journ. Soc. Dyers and Col.*, 1914, **30**, 85-88) that the colouring matter of linen was abnormal in its behaviour towards bleaching agents, but this point was disputed (Higgins, *ibid.*, 1914, **30**, 257). The conclusion was drawn that as regards textile bleaching operations hypochlorites bleach because they produce (1) oxygen directly and (2) some nascent chlorine at the beginning of the action. The latter production will be discussed later, but here it might be mentioned that some confusion was caused because the two experimenters were working with different materials. One was using bleaching solutions prepared in the laboratory and cloth which had not been prepared in any special way, while the other used

the bleaching liquors used in industrial work (which were approximately of constant composition) and well-scoured cloth such as is bleached by the ton every day in bleach-works. In short, Higgins performed his experiments under actual bleaching conditions and formed conclusions after trials in imitation of industrial bleaching.

The Action of Metallic Oxides on Bleaching Solutions

It is well known that the more stable a hypochlorite solution is in air the less readily it bleaches, and any circumstances which make the solution less stable increase its bleaching efficiency. Thus, the addition of alkali increases the stability and decreases the bleaching efficiency. The effect of sunlight on hypochlorite solutions was found by White (*Journ. Soc. Chem. Ind.*, 1903, 132) to produce pure oxygen, or rather the evolution of oxygen from hypochlorite solutions was found to be greatly accelerated by exposure to the sun's rays. All bleachers know the value of the sun's rays in the bleach-house, because they stimulate the bleaching action of hypochlorites; this increased efficiency again forms a parallel with decreased stability, and points to the conclusion that the pure oxygen which is evolved in the one case performs the bleaching in the other. It was further found (Higgins, *Journ. Soc. Dyers and Col.*, 1913, **29**, 85-89) that any agency, such as heat, addition of alkali or acid, and exposure to air, which increased or decreased the rate of production of oxygen when the bleaching-powder solution was in contact with copper oxide, also increased or decreased the bleaching efficiency of that solution, thus pointing to the conclusion that the action of hypochlorites in bleaching cisterns is identical with their action on exposure to air or in contact with copper oxide. In short, the oxidisable matter in the bleaching cistern merely uses up the oxygen which in the other cases is evolved as gas. This analogy is further supported by the observation (Higgins, *Journ. Soc. Chem. Ind.*, 1911, **30**, 185) that copper oxide in contact with the linen fibre during bleaching causes over-bleaching in some cases; the oxygen which does the bleaching is produced too rapidly

and in some cases oxidises the cellulose of the fibre. The oxides of copper, iron, cobalt, manganese, and chromium were found to accelerate the evolution of oxygen from bleaching-powder solution, whereas the oxides of zinc and magnesium were inactive; and it is also known that these oxides behave in a like manner as regards the production of oxygen on heating with potassium chlorate. The analogy was well brought out in some cases. For instance, during the action of manganese dioxide on bleaching-powder solution the solution became violet owing to the formation of permanganate, and it is known that during the heating of potassium chlorate with manganese dioxide a violet colour is sometimes noticed. Again, with chromic oxide bleaching-powder solution gave off a mixture of oxygen and chlorine, a chromate being formed in solution, and it is known that chromic oxide causes the evolution of some chlorine on adding to heated potassium chlorate, the mass also turning yellow owing to the production of chromate (Higgins, *Journ. Soc. Dyers and Col.*, 1912, **28**, 30).

Elledge (*Journ. Ind. Eng. Chem.*, 1916, **8**, 780) states that the pink colour of hypochlorite solutions is not due to ferrates, as previously stated, but to the presence of permanganates.

Bleaching a Unimolecular Action

It has been stated above that hypochlorites bleach because they give up oxygen directly, and in the case of weak solutions this was proved because the action could be represented by the statement

$$\frac{1}{t}\log\frac{a}{a-x} = \text{approx. a constant.}$$

In support of the above conclusion we have the following observations: Lewis (*Chem. Soc. Trans.*, 1912, **101**, 2371) found that the evolution of oxygen from hypochlorite solutions under the action of light was a unimolecular action; Bell (*Zeit. anorg. Chem.*, 1913, **82**, 145) showed the decomposition of bleaching-powder solution by small quantities of cobalt nitrate was a

unimolecular action; Lemoine (*Bull. Soc. Chem.*, 1913, [iv.], **13**, 5) found that the decomposition of dilute solutions of hydrogen peroxide on heating was practically a unimolecular action; and L. Vallery (*Comptes Rend.*, 1916, 326) states that very dilute solutions of hypochlorites decompose slowly, the velocity of decomposition being apparently represented by a portion of an equilateral hyperbola.

The Action of Neutral Salts on Bleaching Solutions

It was shown (Higgins, *Chem. Soc. Trans.*, 1912, **101**, 222; 1911, **99**, 858; *Journ. Soc. Chem. Ind.*, 1913, **32**, 350; *Journ. Soc. Dyers and Col.*, 1913, **29**, 85-89) that neutral salts had an effect in stimulating the bleaching action of hypochlorite solutions, but that this effect was small. Thus sodium chloride, sulphate, and nitrate stimulated the action of sodium hypochlorite on boiled linen cloth; sodium sulphate increased the bleaching efficiency of potassium hypochlorite, and sodium fluoride and calcium nitrate had a like action on bleaching-powder solution. It was also found that the presence of sodium chloride, sulphate, and nitrate all had an accelerating influence on the oxidising action of potassium permanganate on oxalic acid and its bleaching action on linen cloth. Experiments were performed to ascertain the effect of neutral salts on solutions of the hypochlorites of sodium and calcium during the bleaching of dilute solutions of the following dye-stuffs: methyl orange, a basic blue, alizarine sapphirole B and acid violet HW. It was found that sodium chloride, sodium fluoride, calcium chloride, barium chloride, and potassium bromide all had a stimulating effect on the bleaching action of the hypochlorites. In each case it was noticed that the action of the neutral salt was a sudden one; on allowing the solutions to stand, the solution containing no neutral salt gradually became fainter and fainter in colour, then colourless, while the solution containing the neutral salt was still faintly coloured. This was a remarkable observation and will be referred to later, but here it is interesting to mention that B. Fraas (*Papierfabr.*, 1910, **8**, 62) had noticed in some

tests comparing electrolytic bleaching liquor with bleaching-powder solution that the former, which contained a large excess of sodium chloride, was a much more active bleaching agent than the bleaching-powder solution at the commencement of the action, but that the latter acted the more rapidly after this initial effect.

Other neutral salts were tried and sometimes gave peculiar results. For instance, sodium nitrate stimulated the action of bleaching-powder solution on the basic blue dye-stuff but retarded its action on the alizarine sapphirole B until a reddish colour was produced, after which stage an acceleration was noticed.

Using chlorine water as the bleaching agent instead of hypochlorite solution, the following results were obtained:

Salt added.	Dye-stuff.			
	Methyl Orange.	Basic Blue.	Aliz. Sapphirole.	Acid Violet HW.
Sodium chloride .	Acceleration	Acceleration	Acceleration	Acceleration
Calcium chloride .	do.	do.	do.	do.
Hydrochloric acid	do.	No effect	Retardation	do.
Mercuric chloride	Faint acceleration	do.	No effect	No effect
Sodium fluoride .	No effect	Retardation	Retardation	Retardation

Using hypochlorous acid instead of the chlorine water very similar results were obtained, thus supporting the statement (Higgins, *Chem. Soc. Trans.*, 1912, **101**, 222) that chlorine water probably owes its bleaching properties to the presence of hypochlorous acid in solution.

The Action of Chlorides in the Bleaching Process

It has been shown above that chlorides stimulate the bleaching action of hypochlorites, chlorine water, and hypochlorous acid; that chlorides stimulate the action of hypochlorite solutions had previously been stated by Knecht.[1] This action of chlorides was further investi-

[1] *Manual of Dyeing*, Knecht, Rawson and Loewenthal (C. Griffin & Co., London).

gated. As from the tests described above it is seen that chlorides acted upon chlorine water in precisely the same manner as they did on hypochlorous acid, and since chlorine water is unstable in air and difficult to estimate quantitatively, the tests were performed with hypochlorous acid and hypochlorite solutions only. The effect of adding common salt to a solution of potassium hypochlorite used for bleaching well-scoured linen cloth is shown in the following table (*Journ. Sci. Dyers and Col.*, 1913, **29**, 85):

	Potassium Hypochlorite.	
	Alone.	+ Salt.
Original . .	5·55	5·55
After 15 mins. .	4·8	4·6
„ 30 „ .	4·6	4·35
„ 45 „ .	4·4	4·2
„ 60 „ .	4·35	4·1
„ 3½ hours .	3·65	3·45
„ 46 „ .	1·25	1·05

The exhaustion of the baths was tested by withdrawing small samples at the intervals stated, adding potassium iodide and hydrochloric acid, then titrating with decinormal sodium thiosulphate solution. It is noticed that the stimulation produced by the common salt occurs entirely during the first fifteen minutes of the action, after which period there is a steady parallel action in the two solutions.

Higgins (*Journ. Soc. Chem. Ind.*, 1911, 185) pointed out that the addition of chlorides to hypochlorite solutions had but a small effect under actual industrial conditions of bleaching, but in some cases, on a laboratory scale, the effect is apparently large, as judged by the appearance of the bleached cloth. On allowing the action to proceed, this sudden initial effect is seen to be of little consequence. Ricci (*Journ. Soc. Chem. Ind.*, 1915, 714) combats the statement of Cattania and Ranucci (*ibid.*, 1915, 489) that common salt has a large effect on the stability of sodium hypochlorite solutions, but these workers have apparently been investigating hypochlorite solutions prepared by different methods.

Further tests gave the following results:

	Bleaching-powder Solution. Alone.	+ Cal. Chloride.
Original . .	4·2	4·2
After 5 mins. . .	3·9	3·7
„ 10 „ . .	3·7	3·5
„ 15 „ . .	3·55	3·35
„ 30 „ . .	3·35	3·15
„ 1½ hours . .	2·95	2·75

These figures show in a remarkable manner that the initial stimulation has no effect on the subsequent action.

With hypochlorous acid as the bleaching agent the following results were obtained, again using well-scoured linen cloth in the bleaching solution.

	Hypochlorous Acid. Alone.	+ Sod. Chloride.
Original . .	2·8	2·8
After 15 mins. . .	1·9	1·3
„ 30 „ . .	1·65	1·05
„ 75 „ . .	1·3	·7

Again it is noticed that the effect of the chloride is an immediate one, after which it has no further effect.

To explain the stimulating action of chlorides Higgins put forward V. Tiesenholt's equation (*Journ. pr. Chem.*, 1906, **73**, 301):

$$HOCl + NaCl = 2Cl + NaOH.$$

In the case of hypochlorous acid the production of the nascent chlorine gives a sudden stimulation to the bleaching action, but when a new position of equilibrium is produced the action ceases; the bleaching action of the hypochlorous acid is then due to oxygen directly produced:

$$HOCl = HCl + O.$$

In the case of hypochlorite solutions it is known that they contain free hypochlorous acid, because Taylor (*Journ. Chem. Soc.*, 1910, **97**, 2541) found on passing air free from

carbon dioxide through them hypochlorous acid was driven out of solution. On adding chlorides to these solutions during bleaching the stimulation caused is due to the production of nascent chlorine, thus:

$$2HOCl+CaCl_2=Ca(OH)_2+4Cl.$$

But this reaction results in the production of free lime, which, as it accumulates in solution, reacts along with the other lime present and tends to reverse the above action. Before the addition of the chloride the bleaching-powder solution already contained calcium hypochlorite, calcium chloride, hypochlorous acid, and calcium hydroxide in a state of equilibrium, and the addition of more calcium chloride results in a new state of equilibrium being established at the expense of the generation of some chlorine. The production of nascent chlorine accounts for the stimulation of the bleaching action, and the fact that equilibrium is soon again established accounts for the observation that this stimulating effect is a momentary and not a continuous one.

The Bleaching Action of Chlorine Water and of Hypochlorous Acid

Chlorine acts on water in the following manner, according to Jakowkin (*Z. Phys. Chem.*, 1899, **29**, 613):

$$Cl_2Aq+H_2O \rightleftharpoons (HCl+HOCl)Aq,$$

the action being reversible. Chlorine water was found (Higgins, *Chem. Soc. Trans.*, 1912, **101**, 222) to have a feeble bleaching action on the colouring matter of linen, and it therefore seemed probable that the bleaching power of chlorine water was due to the presence of hypochlorous acid in its solution.

On adding boric acid to bleaching-powder solution hypochlorous acid is liberated, as can be proved by distillation, whereas on adding hydrochloric acid chlorine is evolved. Using the solutions prepared in this way as sources of hypochlorous acid and of chlorine water, Higgins (*Journ. Soc. Dyers and Col.*, 1913, **29**, 85-89) showed that

the solution containing the boric acid had a far more energetic bleaching action on the colouring matter of linen than the solution containing the hydrochloric acid.[1] On now dividing the solution containing the free chlorine into two parts and to one adding powdered calcium carbonate, it was found that the addition of the carbonate greatly increased the bleaching properties of the solution. Taking chlorine water as a mixture of hydrochloric acid and hypochlorous acid in equilibrium, the carbonate would act on the hydrochloric acid and thus give the hydrochlorous acid freedom to act.

The bleaching action of hypochlorous acid can only be due to oxygen directly produced:

$$HOCl = HCl + O.$$

The bleaching action of hypochlorite solutions has also been shown to be due to the direct production of oxygen and, in the case of the addition of chlorides, to a small amount of nascent chlorine initially produced by the action of the chlorides on free hydrochlorous acid present in the hypochlorite solution.

The addition of acids and alkalis greatly affects the bleaching properties of hypochlorite solutions. Also on adding small quantities of sodium carbonate and of sodium bicarbonate to sodium hypochlorite solution a slightly decreased bleaching efficiency was noticed (Higgins, *Journ. Soc. Dyers and Col.*, 1914, **30**, 326). The bicarbonate had less effect than the carbonate. The introduction of hydroxyl ions in each case hindered the hydrolysis of the hypochlorite, and thus diminished the amount of free hypochlorous acid in the solution. By cautiously adding small amounts of hydrochloric acid the production of hypochlorous acid was assisted and the bleaching effect of the solution largely increased; by adding lime and sodium hydroxide a steady retardation of the bleaching action was caused, but even a large quantity of the latter did not completely inhibit the

[1] On testing the effect of these two solutions on different dye-stuffs, however, the same conclusion could not always be drawn. Thus alizarine sapphirole was the more affected by the solution containing the boric acid, but cloth dyed with indigo and turkey-red was more rapidly attacked by the solution containing the excess of hydrochloric acid.

action. Reviewing the whole of these observations, Higgins (*Journ. Chem. Soc.*, 1913, **29**, 302) pointed out that bleaching-powder solution to which an excess of boric acid had been added had a very energetic bleaching action on the colouring matter of scoured linen cloth, because the boric acid merely liberates hypochlorous acid from the hypochlorite, whereas an excess of hydrochloric acid produces free chlorine and a solution of weak bleaching properties. If, however, calcium carbonate be added to the latter solution, hypochlorous acid is regenerated and the bleaching properties restored. The addition of hydroxides to hypochlorite solutions opposes the hydrolysis of the hypochlorite and retards the bleaching action, whereas the cautious addition of small quantities of mineral acids assists hydrolysis and stimulates the bleaching action; the effect on the bleaching properties of the solution is due to the active mass of the free hypochlorous acid present being in the one case reduced and in the other augmented. Even in the presence of a large excess of hydroxide the solutions have a small bleaching effect, probably owing to a small amount of hypochlorous acid being still present.

C. Beadle and H. P. Stevens (*Journ. Soc. Chem. Ind.*, 1914, **33**, 727), referring to the above researches, state: "Quite a number of papers have recently been published on the subject of the relative bleaching efficiencies of the hypochlorites. The conclusions arrived at, in most cases, are in our opinion most erroneous. First of all, there has only been one kind of material experimented upon, and another material might have led to quite a different order of so-called efficiencies. Secondly, the relative efficiencies have been expressed as chlorine consumption per unit of weight of raw material on the assumption that the same bleaching effect is always accompanied by the same chlorine consumption, the higher the figure in unit time the greater the so-called efficiency. As a fact, the reverse is the case. The relative efficiencies of all hypochlorite solutions should be judged by the amount of chlorine consumed per unit of effect, and the smaller the chlorine consumption the greater the efficiency. Thus the solution produced by the Hermite electrolyser was

found to be much more effective than the ordinary bleaching powder solution, because the chlorine consumption per unit of bleaching effect was so much less than with ordinary bleaching powder solution." In the discussion on the above paper the importance of the observation (p. 54) that free chlorine had little effect on the colouring matter of linen was emphasised, and experiments on other fibres were promised. If some experiments on other natural colouring matters are now performed (as carefully as the present author has investigated the action on the colouring matters of cotton and linen), then we can hope for progress in the direction of understanding what goes on during industrial bleaching actions. Cotton and linen were investigated because they are practically the only fibres with which the bleacher has got to deal. At any rate, it must be admitted that the other remarks in the above-mentioned paper do not help us at all. In every bleaching trial, which the present author has described, the colour of the bleached cloth was always considered before a conclusion was arrived at; in every case the conclusion formed depended on that colour. The introduction of such vague terms as "chlorine per unit of bleaching effect" was rigorously avoided because each test was treated as a definite chemical reaction and estimated as such. Fanciful properties were not attributed to different forms of "active" chlorine, because he had previously shown that such a position could not be defended, and that it was wrong to endow hypochlorites produced by electrolysis with marvellous properties (p. 73).

The Bleaching Properties of the Hypochlorites of the Alkali Metals.

The statement that the hypochlorites of the alkali metals possess different bleaching properties, the base to which the hypochlorite is united playing an important part in the bleaching action, was found to be erroneous (Higgins, *Chem. Soc. Trans.*, 1912, **101**, 222), at least, when solutions of these hypochlorites were prepared by the exact precipitation of bleaching powder solution by

the carbonates of the alkali metals. Calcium hypochlorite solutions were found to be slightly more active than the hypochlorite solutions of the alkali metals prepared from it, because the carbon dioxide of the air precipitates the free lime from them, whereas, by the action of the carbon dioxide of the air on the other solutions, soluble carbonates are produced, which remain in solution and slightly retard the bleaching activity. If bleaching powder solution be precipitated by magnesium sulphate, the free lime of the solution is thrown down as magnesium hydrate, so that the supernatant liquid contains magnesium hypochlorite and no hydroxyl ions. The magnesium hypochlorite is therefore an extremely active bleaching agent, but this activity has no connection with the fact that the base of the hypochlorite is magnesium.

The stability of hypochlorite solutions is discussed by M. L. Griffin and J. Hedallen (*Journ. Soc. Chem. Ind.*, 1915, **34**, 530). The sludge, after dissolving bleaching powder, contains—

	Sludge.	Original Bleaching Powder.
	Per cent.	Per cent.
CaO	81·0	96·5
MgO	5·5	1·0
Fe_2O_3, Al_2O_3, SiO_2	13·5	2·5

Alumina and magnesia have no effect on the stability of bleaching powder solution provided the latter has a 10 per cent excess of calcium hydroxide; but ferric hydroxide rapidly reduces the availability of the solution (see p. 57). Both the alkaline earths and the alkali metals give practically equally stable hypochlorite solutions (thus confirming the conclusions expressed above), with an availability above 98 per cent after three days' standing. The stability depends on the excess of free alkali, and this also applies in the case of the addition of magnesia. The stability of bleaching powder solution depends very little on its concentration, and even high temperatures have very little effect on the availability.

The stability of bleaching powder solution in air was discussed by Higgins (*Chem. Soc. Trans.*, 1911, **99**, 859). The calcium carbonate deposited was weighed when it was

found to be produced from the calcium of both the free lime and the calcium hypochlorite. After the fifth day of exposure it no longer liberated iodine from potassium iodide.

Original solution	10 c.c.	=	16·55 c.c.	thiosulphate.
After 1 day's exposure	„	=	16·4	„
„ 2 days' „	„	=	13·7	„
„ 3 „ „	„	=	2·6	„

The solution retained its greenish colour up to the end of the second day, but then became colourless, decomposed rapidly, and was no longer alkaline to litmus. On making bleaching trials with the exposed solution, it was found that two days' exposure did not appreciably affect the bleaching efficiency; but after the third day the solution had very marked bleaching properties. These figures show that the method of exposing bleaching powder solution to air, in order to increase its bleaching efficiency, is not a good one, for by the time this purpose is achieved the liquid has lost a very large proportion of its active chlorine. This procedure was used by some bleachers at one time, but abandoned for the reasons stated. It was resuggested by R. L. Taylor (*Chem. Soc. Trans.*, 1910, **97**, 2541), but later (*Journ. Soc. Dyers and Col.*, 1917, **33**, 246-250) he suggests keeping bleaching powder solutions enclosed and away from the action of light.

A very active solution of sodium hypochlorite was produced by Higgins (*Journ. Soc. Dyers and Col.*, 1912, **28**, 30) by precipitating bleaching powder solution by a mixture of sodium carbonate and sodium bicarbonate. On adding sodium bicarbonate to a solution of calcium chloride, calcium hydrogen carbonate is first produced, but decomposes, giving off carbon dioxide and precipitating calcium carbonate. If bleaching powder solution be substituted for the calcium chloride the carbon dioxide evolved unites with the free lime in the solution, precipitates it, and thus produces a very active bleaching liquor. Only a very small amount of sodium bicarbonate is required along with the sodium carbonate.

The High Activity of Old Chemics

When hypochlorites are used in bleaching they become reduced to chlorides, so that there is an accumulation of this salt in old bleaching liquors, which will have some stimulative action on these liquors as shown (p. 59). On examining a sample of old liquor, however, Higgins (*Journ. Soc. Dyers and Col.*, 1912, **28**, 30) found it contained only 5 per cent of calcium chloride, and bleaching trials showed that this small amount of chloride had practically no effect as a stimulant. But these liquors were found to give a precipitate with lime water, hence, by removing the free lime from bleaching powder solution used to replenish the liquors, they would cause a great increase in the bleaching action. J. F. Briggs (*Journ. Soc. Chem. Ind.*, 1916, **35**, 78) states that old chemics contain calcium bicarbonate in solution and calcium carbonate as a sediment. A ripe hypochlorite liquor is acid to phenolphthalein and basic to methyl orange. Such liquors are very valuable for breaking down and eliminating impurities, but in the final chemic, where the object is to clear up the colour of a purified cellulose, it is safer and more satisfactory to employ a more basic bath prepared with fresh bleach liquor.

It is known that these liquors after being in use for some time become so active that caution is required in using them, and it is manifest that the increase in activity is cumulative. Suppose the accelerating effect caused by bleaching a certain weight of cloth be represented by 1 unit. The cloth, on being led into the solution, brings with it a definite amount of water, and, on leaving it, takes away a definite amount of the solution. This causes a dilution of the solution. Suppose the dilution be represented by a; that is, after the bleaching of one lot of goods, say a day's bleaching, the liquor is diluted to a owing to the water brought in.

Then we have:

First day. Increase in bleaching effect = 1 unit, which is decreased to a by dilution.

Second day $= 1 + a$. *i.e.* 1 unit + first day's effect.

Third day $= 1 + a(1 + a)$.

Fourth day $= 1 + a\{1 + a(1 + a)\}$.

A simple algebraic summation shows that after the nth day the increase in effect is:

$$n\text{th day} = \frac{(1-a)^n}{1-a}.$$

Now if $a = \frac{10}{11}$ then after the ninth day the increase in activity is represented by 5 units, and this increase may become as high as 11 units, at which stage the liquors must be used with caution. But by regulating the value of a, safe bleaching can be assured, and the liquor may never be run to waste.

L. T. Thorne (*Journ. Soc. Chem. Ind.*, 1914, **33**, 729) states that by introducing oxygen gas during the bleaching of paper pulp the consumption of bleaching powder could be reduced from 30 to 50 per cent, and the oxygen of the air was said to also have a large effect. "Reeling" and circulating the chemic during the bleaching of textiles would have a similar effect, but there is also the action of the carbon dioxide of the air to be considered.

The *analysis of hypochlorite solutions* is described by J. Clarens (*Ann. Chem. Analyt.*, 1915, **20**, 81). All hypochlorite solutions contain chlorites, which react with hypochlorous acid to form chlorates and chlorine peroxide. This accounts for the lower results (about 2%) obtained by Penot's method of titration with sodium arsenite solution using starch-iodide paper as the indicator, as compared with those calculated from the amount of gas liberated by interaction with hydrogen peroxide, or by Mohr's modification of adding an excess of arsenite and titrating with standard iodine solution. The author suggests the following method. Add the arsenite required in Penot's original method at once to the hypochlorite; the liquid will still give a blue colour with the starch-iodide paper, and the titration is completed with the standard arsenite until the paper ceases to turn blue. M. L. Griffin and J. Hedallen (*Journ. Soc. Chem. Ind.*, 1915, **34**, 530) found Penot's and Mohr's methods gave concordant results which were in every case about 0·6 per cent lower than those obtained by Bunsen's method of adding potassium iodide and acetic acid, then titrating with sodium thiosulphate solution.

K. J. P. Orton and W. J. Jones (*Analyst*, 1909, **34**, 317) estimate the alkalinity of bleaching powder solutions by adding a measured volume of N/10 hydrochloric acid, passing a current of air through the solution until all the chlorine is driven off, then titrating the excess of acid with N/10 sodium carbonate. The titre of the bleaching powder solution with N/10 thiosulphate gives directly the volume of N/10 acid reacting with the hypochlorite, the alkalinity of the solution being represented by the difference between this and the total volume of the acid used up.

W. Mestrezat (*J. Pharm. Chim.*, 1919, **20**, 9-14) determines the free alkali and alkali carbonate in hypochlorite solutions by adding sodium thiosulphate to destroy the hypochlorite, then titrating the alkali and alkali carbonates directly.

It is interesting here to note the conclusion of E. Justin-Mueller (*J. Pharm. Chim.*, 1919, **20**, 113) that alkali hypochlorites and bleaching powder have similar chemical formulae, a conclusion formed after observations on the reactions of these bodies, and the statement of A. H. Meldrum (*Journ. Soc. Chem. Ind.*, 1919, 80) that bleaching powder is more rapidly dried in desiccators by means of alkaline agents such as sodium hydroxide or basic calcium chloride, the tendency of bleaching powder to lose available chlorine being much reduced by desiccation. Bleaching powder loses chlorine in addition to water during the drying process, and this chlorine is absorbed by the alkaline drying agents.

Bleaching Agents and Antiseptics

During the war hypochlorites have been found very efficacious as antiseptics, and Higgins (*Journ. Soc. Dyers and Col.*, 1918, **34**, 189) shows that all the hypochlorite mixtures which have been used he had previously used as bleaching agents. Lorrain Smith, Drennan, Rettie, and Campbell (*Brit. Med. Journ.*, July 1915) state that "hypochlorous acid is a more effective antiseptic than hypochlorites, and, as already arrived at by various investigators, it is the most powerful antiseptic known." It had previously been shown that it is the most

powerful of bleaching agents (*Journ. Soc. Dyers and Col.*, 1914, **30**, 326-328). H. D. Dakin (*Brit. Med. Journ.*, 1915, **2**, 318) described an antiseptic solution containing sodium hypochlorite and sodium bicarbonate, which mixture had previously been used for bleaching (*Journ. Soc. Dyers and Col.*, 1912, **28**, 30. See p. 67). A mixture of bleaching powder and boric acid has also been used (see Rettie, *Journ. Soc. Chem. Ind.*, 1918, **37**, 23) as an antiseptic, and had previously been used as a bleaching agent (Higgins, *Journ. Soc. Dyers and Col.*, 1914, **30**, 257-261. See p. 63). By adding boric acid to electrolysed salt water an antiseptic of great power would be obtained, besides having a cleansing effect in wound treatment, because of the undecomposed salt it contained. J. J. Rettie, J. L. Smith, and J. Ritchie (*Journ. Soc. Chem. Ind.*, 1918, 392, R) suggest mixing freshly ignited quicklime with bleaching powder intended for export to hot countries, since in this way the loss of available chlorine is largely avoided and the formation of calcium chlorate inhibited. It is known that the addition of hydroxides to hypochlorites increases their stability, and in the case of bleaching powder this fact is also expected to hold, since the powder is hygroscopic; but it must also be remembered that the addition of hydroxides, while increasing the stability, also decreases the bleaching properties of hypochlorites, and also, from what has been stated above, the addition decreases the antiseptic properties. The lime which is added to the bleaching powder could not be separated when it has served its purpose, and the solution produced would have weaker bleaching and antiseptic properties because of the presence of the lime.

The addition of bicarbonate of soda to bleaching liquor has recently been suggested by J. E. Macilwaine (Eng. Pats. 28911 and 6317). The idea is to impregnate the cloth with a solution of sodium bicarbonate and then run it into the bleaching powder solution. Higgins (*Journ. Soc. Dyers and Col.*, 1912, **28**, 30) had shown that, by adding sodium carbonate mixed with a little bicarbonate to bleaching powder solution, the supernatant liquid was a very active bleaching agent (p. 67), and if this reaction takes place on the cloth the great bleaching effect will

result. At the same time, however, calcium carbonate will be deposited on the cloth, and this insoluble matter will have to be eliminated by treatment with acid. Now suppose the cloth be run through weak hydrochloric acid instead of the bicarbonate solution. The result will be exactly the same, with the additional advantage that no insoluble calcium carbonate will be produced, requiring acid to eliminate it. This is an old method of procedure among bleachers, and, carefully performed, it is preferable to the newly described one.

M. Freiberger (*Färber Zeit.*, 1919, **30**, 89-94) describes a number of experiments on the bleaching of cotton cloth with various bleaching agents, and arrives at the conclusion that the addition of sodium carbonate to bleaching powder solution has, up to a certain limit, a beneficial effect on the bleaching action of the solution. This statement, however, is not in accordance with experiments described above, which show that the addition of sodium carbonate to sodium hypochlorite solution has a small retarding effect on the bleaching action of the latter solution, for the introduction of hydroxyl ions hinders the hydrolysis of the hypochlorite and thus diminishes the amount of hypochlorous acid present in the solution. His statement that the replacement of calcium by sodium hypochlorite produces a less energetic bleaching action is not in accordance with the results described, for if the calcium be exactly precipitated by sodium carbonate the bleaching liquor obtained has bleaching properties identical with those of the original bleaching powder solution. Freiberger again states his preference for warm hypochlorite solutions, which, he says, give more permanent whites, and if used strong, deposit calcium carbonate in a fine powder instead of the crust produced by cold solutions. His work seems to indicate that from a few laboratory experiments he attempts to make broad generalisations to affect the whole bleaching industry. His conclusions, however, should be taken *cum grano salis*.

CHAPTER VIII

HYPOCHLORITES PRODUCED BY ELECTROLYSIS

Alkalinity of electrolytic liquor—Comparison with bleaching powder solution—Methods of increasing the active chlorine strength—Other methods of production.

By the electrolysis of common salt solution hypochlorites are now prepared. The first products of the electrolysis are sodium and chlorine, then the sodium reacts with the water to produce hydrogen and caustic soda, and the chlorine reacting with the caustic soda produces chloride and hypochlorite of sodium. The hydrogen is evolved, and in some electrolysers this evolution is used to produce the circulation of the electrolyte. With perfect circulation a neutral product would be expected ; actually, however, the resulting solution is always slightly alkaline, because the caustic soda produced is completely retained by the solution, whereas some of the chlorine, which unites with the caustic soda to produce substances of a neutral reaction, escapes. The better the circulation in the electrolyser, the more the chlorine is retained and the less the alkalinity of the solution.

Many outrageous statements have been made concerning the properties of electrolytically-prepared hypochlorite solutions, the active chlorine of which is endowed with fanciful properties, which are often described but never proved ; and in spite of work carefully conducted to show the fallacy of such contentions, these ideas have been retained up to quite recent times. For instance, C. Beadle (*Journ. Soc. Chem. Ind.*, 1908, 264) states that 3 lbs. of chlorine in the case of Hermite liquor is equal in bleaching effect to 5 lbs. of chlorine in the case of bleaching powder, the rate of efficiency being therefore 3 : 5.

The present author was at one time much impressed with the idea of making bleaching solutions by electrolysis, and he obtained an electrolyser of the best type for experiment. After many months' working, to give it a fair trial, this electrolyser is now idle. The attention required was far greater than in the case of dissolving bleaching powder, and no economy was recorded (Higgins, *Journ. Soc. Chem. Ind.*, 1911, 185). Electrolytically prepared sodium hypochlorite was found to be almost identical in its properties with bleaching-powder solution. There was no appreciable difference in the stability in air on prolonged agitation or on acidifying. Material bleached by it showed no difference in appearance or in tensile strength, nor did the rate of bleaching exceed that of bleaching-powder solution. As regards the relative costs of the two bleaching solutions, everything depends on the cost of salt and of current at different works. In some districts the cost of the salt alone might be as high as the total cost of the bleaching powder the electrolyser seeks to displace; and similarly a high cost of current would place the method of producing bleaching solutions out of consideration.

J. B. C. Kershaw (*Journ. Soc. Chem. Ind.*, 1912, **31**, 54) states that "the reason the electrolytic method of producing hypochlorites has not been adopted by the large and important bleaching interests of Lancashire and Yorkshire is made apparent when one studies the tabular statements of comparative costs and effects deduced by Higgins (*loc. cit.*) from the experiments made with various forms of bleaching solutions. It is now generally recognised that there is but slight difference between the bleaching effects obtained." Allan Smith (*Journ. Soc. Chem. Ind.*, 1916, 281) states: "I have made a very exhaustive test on a big scale, in which many tons of material were bleached at the same time, one by a solution of bleaching powder, and one by sodium hypochlorite prepared by an electrolyser, and I found the same or practically identical results in both cases." Roscoe and Lunt found on electrolysing sea water that the hypochlorite decomposed rapidly. This decomposition was evidently caused by the weak solution oxidising the impurities of the sea water, for stronger

solutions did not decompose so rapidly, nor did weak ones made by diluting strong ones with distilled water. Doninelli (*Rev. Gen. Mat. Col.*, 1911, **15**, 341) found that hypochlorites produced by electrolysis were often strongly alkaline. In such cases the circulation in the electrolyser must have been very poor, the chlorine gas escaping instead of reacting with the caustic soda. A. Ahlin (*Papier Zeit.*, 1908, **33**, 834) concludes that the only difference between electrolytic liquor and ordinary bleaching liquor is the slightly more rapid action of the former; the consumption of chlorine for a given amount of bleaching work done is very slightly lower on this account. It is shown on page 59 that chlorides give a slight stimulation to the bleaching action of hypochlorites, a fact which was first observed by Knecht; and as electrolytic bleaching liquors contain a large amount of unaltered chloride there is in some cases a momentary stimulation on this account.

The claim that goods bleached by hypochlorites prepared by electrolysis do not turn yellow in stock cannot be upheld, because, as shown on p. 36, this deterioration is not due to a deficiency in the bleaching agent, but to inefficient scouring. Bleachers object that electrolysers do not yield solutions strong enough for some of their work. By adding lime and calcium chloride to the salt solution during electrolysis it is claimed that a liquor containing more hypochlorite is produced, but in this case one of the advantages of sodium hypochlorite, namely, absence of lime salts, is lost.

Beltzer (*Z. angew. Chem.*, 1907, **22**, 8-14) uses strong brine solutions for electrolysing, because the conductivity of the solution increases with the concentration; and in order to increase the stability of electrolytically prepared hypochlorite solutions, F. W. Alexander (*Lancet*, Jan. 18, 1908) adds magnesium oxide (or hydroxide). Being insoluble it does not cause strong alkalinity as caustic soda does.

F. D. Toyne (*Journ. Soc. Chem. Ind.*, 1912, **31**, 477) uses hypochlorites prepared by electrolysis for the treatment of impure water, in order to prevent the staining of textiles by chromogenic organisms, harmful moulds, or algae.

Various attempts have been made to increase the strength of the hypochlorite produced by electrolysis by adding substances to the solution during electrolysis. P. H. Prausnitz (*Z. Elektrochem.*, 1912, **18**, 1025) recommends the addition of chromates as the best protection against reduction; for a high concentration of hypochlorite, with a good current efficiency, it is best to add both chromate and Turkey-red oil, which substances give better results than calcium chloride and resin. By this method a concentration of 62 grms. of active chlorine per litre can be obtained from a 5 N salt solution. The use of Portland cement for the cells is recommended. F. Foerster (*Chem. Ind.*, 1911, **34**, 373-378, 402-413) adds calcium chloride or alkali chromate to the electrolyte, and also some alkali, to counteract the absorption of carbon dioxide. Sometimes calcium chloride and hydroxide and resin soap are added to the liquid to form the cathode diaphragm. He states that installations for separating the caustic soda and the chlorine to produce caustic soda and bleaching powder separately cannot be profitable if they produce less than 5000 tons of the latter compound per annum.

Siemens and Halske, after careful experiment, have come to the conclusion that the direct manufacture of hypochlorites in electrolysers is not the best way of producing hypochlorite solutions. By means of the Billiter cell they produce the caustic soda and chlorine separate and then mix them to give the hypochlorite solution. This they regard as a far better method. The Billiter alkali-chlorine cell is described by A. J. Allmand (*Faraday Soc.*, Nov. 1912), and is stated to have the lowest energy consumption per ton of product of any cell now working on the large scale. Impure brines may be used without filtering, and the concentration of the alkali is from 12 to 16 per cent. V. Engelhardt (*Chem. Zeit.*, 1911, **35**, 573-574, 582-584) discusses the types of plant used for producing caustic soda and chlorine; of the diaphragm, the gravity or "bell" apparatus, and the mercury cathode plant, only the last named produces an alkali solution free from salt. Of the diaphragm type the Billiter is notable, and its advantage over bleaching powder begins when power costs less than 0·4d. per kilowatt-hour. W. Ebert

(*Papierfabr.*, 1911, **9**, 305-308) describes the electrolytic production of caustic soda and chlorine. The salt solution is distributed uniformly by pipes through the covers into the anode chambers of the electrolytic cells. The chlorine gas evolved is used to make bleaching liquor or bleaching powder, the hydrogen gas is allowed to escape or is collected, and the caustic soda is separated from the salt. Per kilo. of active chlorine 3 kilos. of salt are consumed (or 1·6 kilos. of the salt is separated from the caustic soda) against a consumption of 5 kilos. of salt in the production of hypochlorite in an electrolyser. As regards the production of sodium hypochlorite from caustic soda and chlorine, U. Cattania and C. Ranucci (*Annali Chem. Appli.*, 1915, **3**, 161-164) make sodium hypochlorite solution (28° B, sp. gr. 1·241) by the interaction of chlorine and caustic soda in an absorption tower, and find it usually contains 8-9 per cent of available chlorine, but rarely 10 per cent. The authors prepared solutions up to 17·7 per cent by bubbling chlorine into caustic soda solution of 28° B contained in a stoneware vessel provided with an agitator and placed in a tank of cold water, but when the concentration reached 17·7 per cent, separation of sodium chloride commenced. The hypochlorite then gradually decomposed on allowing the solution to stand, but the solutions maintained their strength when the sodium chloride was removed as soon as it separated.

In connection with hypochlorites used for bleaching the claim (*Deutsch. Solvay-Werke Act. Ges.*, Ger. Pat. 306193, 1916) for producing a dilute bleaching liquor by passing chlorine into sodium carbonate solution, then adding more sodium carbonate, is of interest, and also the production of a high-strength bleach by the reaction of steam and chlorine at about 100° C. to give hydrochloric acid and hypochlorous acid, the former being removed by condensation and the latter by absorption in caustic alkali (K. P. M'Elroy, U.S. Pat. 1261572, 1918).

CHAPTER IX

CELLULOSE AND WATER

Effect of boiling water—Effect of caustic soda—Attraction of moisture and of dye-stuffs—Cellulose hydrates—Effect of drying cotton—Colloidal nature of cellulose.

It was shown by J. Hübner and W. J. Pope (*Journ. Soc. Chem. Ind.*, 1903, **22**, 70) that, on boiling cotton for 12 hours in water, its power of attracting direct cotton dye-stuffs (benzo-purpurine, 4 B) was increased, whereas it took up less basic dye-stuff (methylene blue). This effect was more accentuated by heating with water in a sealed tube at 150° C. Mercerised cotton acted in a similar manner; on boiling for 48 hours with water, the cotton gave at least twice as strong a dyeing with benzo-purpurine 4 B. These results show that cotton is altered by the long boiling it is given in industrial bleaching. They also showed that boiling with alkaline solutions increased the tensile strength of cotton yarns. This observation will be referred to later, but it must here be pointed out that other factors are introduced than the change in the cellulose itself. In fact, to compare the effect of bleaching on the cellulose, the fibres alone would have to be considered.

Tauss (*Journ. Soc. Chem. Ind.*, 1889, 93; 1890, 883) found that purified cotton cellulose digested with solutions of sodium hydroxide (3 per cent Na_2O) three times in succession was attacked and converted into soluble products in the following proportions, increasing with the temperature of digestion:

	3 per cent Na_2O.	8 per cent Na_2O.
1 atmos. pres. .	12·1 per cent.	22·0 per cent.
5 „ .	15·4 „	58·0 „
10 „ .	20·3 „	59·0 „

Then it is known that cotton heated with water to 200° C. yields carbon dioxide, formic acid, pyrocatechin, glucose, etc. C. G. Schwalbe (*Chem. Zeit.*, 1910, **34**, 551) states that only celluloses which contain oxycellulose show the property, described by Tauss, of yielding hydrocellulose on heating under a pressure of 20 atmospheres. Pure normal cotton cellulose suffers but a very slight hydrolysis. At temperatures above 100° C. dehydration appears to take place, the "hydration value" decreasing with increase of temperature. The proportion of products soluble in water increases only very slowly with increase of temperature up to 150° C., but it increases very rapidly above that temperature. On heating with sodium hydroxide under pressure the cupric-reducing power of the cellulose, which appears under the action of sodium hydroxide at temperatures below 100° C., disappears when the concentration of the lye is 1-2 per cent; with lyes of higher concentration (3-5 per cent) the cupric-reducing power does not disappear until a temperature of 135° C. is reached. The degree of hydrolysis as expressed by the cupric-reducing power is a maximum with a 4 per cent lye, lyes of 3 per cent and of 5 per cent both having a weaker action. The solubility of cotton cellulose in sodium hydroxide at the ordinary temperature decreases as the concentration of the lye increases, and this is also the case at 100° C. At a temperature of 150° C. the solubility in lyes of 1-5 per cent ranges from 5 to 7 per cent. Above 150° C. the solubility of cellulose increases with extreme rapidity. The temperature of 150° C. may be regarded as the decomposition temperature of cotton cellulose. Relatively, the solubility of cotton cellulose is lowest in 5 per cent sodium hydroxide and highest in the 4 per cent solution. As in the case of water, sodium hydroxide also appears to produce dehydration at temperatures above 100° C., since the "hydrolysis value" decreases with increase of temperature. Egyptian cotton appears to possess a higher "degree of hydration" than American cotton. Schwalbe and M. Robinoff (*Z. angew. Chem.*, 1911, **24**, 256) also found that Egyptian cotton gave much lower "copper values" than American cotton. M. Robinoff (*Papierfabrikant*, 1912, **10**, 968) states

that cellulose which has become modified in industrial bleaching processes possesses totally different properties from normal cellulose. Normal cellulose is extremely resistant and is only slightly modified when boiled with water under pressure, but cellulose which has been subjected to boiling and bleaching processes is very considerably attacked by boiling water under pressure, especially at temperatures above 150° C., and is completely broken down to hydrocellulose when digested under a pressure of 20 atmospheres.

Cellulose and Moisture

Cross and Bevan found on drying cellulose in a current of carbon dioxide at 90° to 100° C. that the hygroscopic moisture (6-8 per cent) is rapidly driven off; on heating to 120° C. a further 0·5 per cent was driven off, and at 180° C. a further 0·5 per cent. After a temperature of 120° C. is attained, the loss is slow and probably due to decomposition. They maintain that the attraction for water is a property of the cellulose substance itself, and is not in any way dependent upon the form in which it occurs. Whether it is chemical or physical cannot be decided. The amount of moisture attracted is definitely related to the number of hydroxyl groups in the cellulose molecule since, as esters are formed by combination with negative radicles, the products exhibit decreasing attractions for atmospheric moisture. It is also to be noted that some of these synthetic derivatives are formed with only slight modification of the external or visible structure of the cell, of which, therefore, the phenomenon mentioned is independent. Orme Masson (*Pro. R. S.*, 1901, **74**, 230), from a close study of the thermal effects, concluded "that the heat produced by the absorption of water vapour by cotton is of about the same magnitude as the heat of liquefaction of the same quantity of water," and "the view that water becomes chemically combined to form definite hydrates of cellulose cannot be supported by facts." He regards the combination as a solid solution of cellulose and water: "the deposited moisture does not all remain as a mechanically adherent film on the surface

of the cotton, but undergoes osmotic diffusion into the substance of the fibres and forms with it what may be regarded as a solid solution of cellulose and water." Cross and Bevan (*Researches on Cellulose*, ii.) suggest that these effects cannot be separated from the general range of hydration changes determined by alkalis, acids, and salts. The influence of the hygrometric state of the celluloses upon the mechanical properties of these aggregates is an evidence of the intrinsic effects of the combined water; and it must be remembered that the structureless forms of cellulose are more sensitive than the "natural" fibrous forms to these influences.

Higgins (*Journ. Soc. Chem. Ind.*, 1909, **28**, 188) noticed that there was a connection between the amount of dye-stuff textile fibres were capable of absorbing from solution and the amount of moisture which those fibres attracted from the air. Mercerised cotton absorbed more dye-stuff from solution and more moisture from the air than ordinary cotton, and this attraction was found to be the greater the stronger the solution of caustic soda used for the mercerisation. If the amounts of moisture and of dye-stuff attracted were plotted along with the degrees Tw. of the caustic soda used, it was found that the curves obtained were of a similar nature. Moreover, it was found that the attraction for moisture was also proportional to the attraction for iodine from potassium iodide solution.

Sample of Cotton.	A Iodine absorbed by 100 grams Dry Material.	B Moisture absorbed by 100 grams Dry Material.	$\frac{B}{A}$
Ordinary unbleached . .	0·3	6·52	21·73
„ bleached . .	0·2896	6·25	21·59
Mercerised without tension	0·4622	9·33	20·19
„ bleached . .	0·4216	9·12	21·63
„ with tension .	0·4136	8·28	20·02
„ bleached . .	0·3556	8·05	22·63

Although a big variation is noticed in columns 1 and 2, it is seen that column 3 contains an approximate constant, thus pointing to the conclusion that the absorption of the

moisture and of the iodine by the cellulose were similar processes. Again, it is known that both mercerised and ordinary cotton after drying for a long time in a stove do not take up as much substantive cotton dye-stuff as they did before drying, and it is also found that they do not take up as much moisture after this drying action. The above results point to an analogy between the absorption by textile fabrics of moisture from the air (*i.e.* a vapour from a gaseous medium) and of dye-stuffs from solution (*i.e.* solids from a liquid medium).

H. Ost and F. Westhoff (*Chem. Zeit.*, 1909, **33**, 197-198), in discussing the so-called cellulose hydrates, mention that Cross and Bevan have applied the name "hydrates" to those modifications of cellulose containing, in addition to hygroscopic moisture, which is dependent on atmospheric conditions, "water of hydration," which is dependent on the constitutional modification, and is more firmly held than ordinary hygroscopic moisture. Thus they have indicated for mercerised cotton the formula $(C_6H_{10}O_5)_{21}H_2O$. In the case of the hydrocelluloses, on the other hand, the cellulose has permanently entered into chemical combination with water to form new derivatives, and such products are termed "hydrates" only in the same sense as the dextrins, maltose, etc., might be termed "hydrates of starch." Schwalbe has endeavoured to distinguish between hygroscopic moisture and water of hydration by assuming that the former is entirely expelled at 100° C., whilst the latter is only driven off at the temperature of boiling toluene, but such a distinction has been found to be invalid. The exact determination of hygroscopic moisture in members of the cellulose and starch groups is a very difficult problem. Small progressive losses of weight are recorded as the temperature of drying is increased from 100° to 130° C., no absolutely fixed point being reached in any case. It is universally recognised, however, that under all conditions of drying the hydrated celluloses, such as mercerised cotton, contain considerably more, and the hydrocelluloses rather less water than the normal cotton cellulose. Ost and Westhoff do not recognise the existence of "water of hydration" as distinct from hygroscopic moisture as a constitutional

component of these modified celluloses, for after expelling the hygroscopic moisture from mercerised cotton by drying at a temperature of 120°-125° C. the cellulose regenerated possessed the same empirical formula as normal cotton cellulose. Cross and Bevan (*Researches on Cellulose*, 1910) criticise Ost and Westhoff's statements, and maintain that the expulsion of water from these colloids is a dissociation. Mercerisation increases the hydrated capacity by a definite proportion, as an ultimate property of the modified cellulose; but the process of mercerisation is a joint reaction of combination with alkali and water, the alkali-cellulose having a very high hydration capacity. They object to the heating of cellulose to 125° C. to drive off the moisture, because the temperature of decomposition of cellulose (160° C.) is being approached.

On the other hand, H. Ost (*Annalen*, 1913, **398**, 313-343) claims that neither cellulose nor hydrocellulose become perfectly anhydrous when dried at 100°-105° C.; the sample should be heated slowly up to that temperature, and finally dehydrated at 120°-125° C. Between that temperature and 130° C. or even 140° C., purified cotton cellulose remains white and suffers no further loss in weight, but certain samples of hydrocellulose are slightly decomposed by heating at 125°-130° C. Hydrocellulose is less hygroscopic than cellulose, but when both substances are corrected for the hygroscopic moisture expelled at 120° C., ultimate analysis fails to show any difference between cellulose and hydrocellulose.

On heating raw fibres to 100° C. or over that temperature, it must not be forgotten that the non-cellulose constituents of the fibre are affected. For example, the proteins are changed as previously pointed out, and the wax in melting covers the fibre in a different manner. Since the purpose of the wax in nature is said to be principally to keep out water, then any change in the form in which the wax exists on the fibre will have some influence on the fibre's power of attracting moisture from the air. Moreover, when the wax is once melted it never returns to its original form of aggregation. Then cotton is said to contain about 0·06 per cent of magnesium chloride, which on heating generates hydrochloric

acid, and might affect the fibres. It is evident, therefore, in dealing with this matter of moisture absorption, one must differentiate between the properties of raw fibres and the properties of fibres of cellulose separated from raw fibres.

E. Knecht (*Journ. Soc. Dyers and Col.*, 1908, **24**, 107-109) describes the following experiments on the effect of drying on the affinity of ordinary and mercerised cotton for dye-stuffs. Cotton yarn was mercerised and some hanks were left wet, others were dried in air, and others were dried in a stove at 110° C. On dyeing these different hanks with benzo-purpurine 4 B, it was found that drying in air had caused a decrease of the affinity for the dye-stuff, and stove drying had had a still more marked effect. This change of affinity seems to be permanent, and prolonged exposure to air or steeping does not seem to restore it. If materials are allowed to dry in places after mercerisation then uneven dyeing will probably result. C. Favre (*Bull. Soc. Ind.*, Mulhouse, 1912, **82**, 183-184) found that high temperatures or steaming change the physical properties of cotton in a manner the reverse of that of mercerising, the cotton being less able to absorb dye-stuffs after steaming. Mercerised cotton loses its power under these conditions of absorbing more dye-stuff than ordinary cotton, without, however, losing its brilliance.

E. Justin-Mueller (*Färber-Zeit.*, 1913, **24**, 98), regards the affinity of cotton for dye-stuffs to be proportional to the colloid activity, which is developed by the moisture normally present in cotton. This moisture may be looked upon as "colloid water" analogous to water of crystallisation in the case of crystalloid substances, and to its presence is due the colloid activity of the cotton. The colloid activity, and consequently the affinity for dye-stuffs, is therefore diminished by the influence of heat and steam, which tend to remove the normally bound water. The prevention of this loss of affinity by moistening the cloth, or by adding hygroscopic substances before steaming, follows. On the other hand, the use of a sufficient quantity of glycerine may result in an increase in affinity by steaming under pressure owing to hygroscopic action.

The influence of moisture on the strength and count of

cotton yarn has been investigated by F. W. Barwick (*Journ. Soc. Dyers and Col.*, 1913, **29**, 13). Cotton yarn was found to vary from 6 to 10 per cent of moisture throughout a period of three months, and assuming the yarn to have been 40's in count, this corresponds to an apparent variation between 41's and 39's. The strength of wool, cotton, and linen cloths depended to a large extent upon the conditions of the atmosphere to which they were exposed. Thus, cotton and linen cloth increased and decreased in strength as the humidity increased and decreased, the variation in strength being as much as 18 per cent. The conditions of temperature and humidity should therefore be standardised for the testing of textiles. Erban (*Z. angew. Chem.*, 1914, **27**, 41) states that in finishing fabrics various machines for applying low temperatures are in use to shorten processes, and to increase the amount of moisture fixed by the fibres.

C. G. Schwalbe (*Z. angew. Chem.*, 1907, **20**, 2166-2172; 1908, **21**, 401-402) describes two methods of determining the water contained in cellulose. In the first paper this determination is made by the use of a toluene drying stove, but in the second paper he uses petroleum. The results he says agree when determinations are made by the two methods. Into a copper retort, which is tinned inside, 50 to 100 grms. of the material are placed and covered by 1·5-2 litres of petroleum. The retort is joined to a tube the narrow part of which is graduated. The retort is heated for ten to fifteen minutes with a bunsen burner, and the apparatus is then allowed to cool during three to four hours; when the liquid in the graduated tube becomes clear, the volume of the water distilled is read off. A correction for the water dissolved in the petroleum can be applied. He gives the following determinations of what he calls "water of hydration":

Cotton cloth	0·23
,, beaten to pulp . . .	1·56
Mercerised cotton (beaten to pulp) . .	6·31
Hydrocellulose	1·2

E. Knecht (*Journ. Soc. Dyers and Col.*, 1920, 195) shows that prolonged action of moderate heat on cotton and

similar materials causes a considerable decomposition of the cellulose. For instance, a temperature of 93° C. for several hundred hours has a pronounced effect, and starch also turns brown when maintained at a moderate heat for a long time.

CHAPTER X

CELLULOSE AND STRONG ALKALIS

Alkali-celluloses—Use of salt in mercerising lyes—Cellulose hydrates—Other mercerising agents—Cold mercerising—Theory of mercerising—Tests for mercerised cotton.

SINCE the researches of Gladstone it was generally understood that cellulose unites with sodium hydroxide to form compounds known as alkali-celluloses. W. Vieweg (*Chem. Zeit.*, 1908, **32**, 329-330) found that cellulose combines with different quantities of sodium hydroxide on treatment with solutions of different concentrations. The maximum quantity entering into combination with the cellulose is reached with a 16 per cent solution, the combining proportions being represented in this case by the formula $C_{12}H_{19}O_{10}$, NaOH. The author proposes that the amount of sodium hydroxide which 100 grms. of cellulose will combine with on treatment with a 2 per cent solution should be known as the "degree of mercerisation" of the cellulose, and that this constant be used as a test for different celluloses. He further states (*Ber.*, 1908, **41**, 3269-3275) that between the concentration of 11 and 24 grms. of sodium hydroxide per 100 c.c. the proportion of the hydroxide removed from solution by cotton approximates to a constant, and corresponds with a definite compound $C_{12}H_{19}O_{10}Na$. The formation of this compound is indicated by a horizontal portion in the absorption-concentration curve. Saturation of the sodium hydroxide solutions with common salt causes an increased absorption of the hydroxide by the cellulose in solutions of equal alkali concentration. Thus, the formation of Gladstone's compound is reached at a lower concentration of sodium hydroxide than when sodium chloride is absent. The salt

is said to have a physical influence, and superimposes an "absorption" of alkali by the cellulose, in addition to the simple chemical combination.

O. Miller (*Ber.*, 1908, **41**, 4297-4304) criticises Vieweg's results, and states that except for very low and very high concentrations of sodium hydroxide, when secondary effects come into play, the ratio of the concentration of the alkali in the solid and liquid phases respectively is approximately a constant. This fact supports his view that alkali-cellulose is a solid solution. He also disputes the existence of horizontal portions in the absorption-concentration curve as described by Vieweg. As an explanation of the effect of sodium chloride, he states that the influence of this salt on the distribution of the hydroxide between the two phases is due to the molecular weight of the hydroxide in the cellulose being greater than in the aqueous chloride solution. J. Hübner (*Journ. Soc. Chem. Ind.*, 1909, **28**, 228), however, found that the addition of common salt to soda lye did not cause cotton to take up more sodium hydroxide. In actual mercerising trials the addition of salt to the soda lye caused less shrinkage of the cotton and less lustre when the cotton was not allowed to shrink. There was also a decreased affinity for substantive cotton dye-stuff, and examination under the microscope showed that the fibres untwisted much less rapidly than in the absence of the salt. A number of tests by Knecht and trials on the large scale also proved that Vieweg's contentions were wrong, and that mercerisers could not use common salt to economise the more expensive caustic soda.

J. Hübner and F. Teltscher (*Journ. Soc. Chem. Ind.*, 1909, **28**, 64) described experiments which did not support the supposed existence of distinct chemical compounds between cotton and sodium hydroxides, sometimes called "soda-celluloses." The amount of the soda held by the cellulose against removal by absolute alcohol was found to be much smaller than that found by Gladstone and other investigators. A. Leighton (*Journ. Phys. Chem.*, 1916, **20**, 32-50) criticises Hübner and Teltscher's experiments, stating that the soda remaining in the cellulose after washing with alcohol is a function of the temperature. He

also states that their data give no indication of the way in which cotton absorbs sodium hydroxide from aqueous solution. But he supports them in the statement that there is no experimental evidence of the formation of any chemical compound of cotton with sodium hydroxide at any stage of concentration, the graphic representation of the results having the form of a perfectly smooth absorption curve.

The question of the existence of cellulose hydrates has been much discussed. Schwalbe (*Z. angew. Chem.*, 1909, **22**, 197-201) regards the hydrated celluloses as differing widely in their properties, but a high hygroscopic moisture is common to all; the hydrocelluloses, on the other hand, are distinguished by an abnormally low moisture content. He contrasts the different methods of determining the "degree of hydration" or, for mercerised cotton, the "degree of mercerisation," and suggests the following method: The "copper value" of the sample is first determined. Then another portion is boiled with a standard quantity of 5 per cent sulphuric acid for fifteen minutes. The acid is neutralised and the prescribed quantity of Fehling's solution is added to determine a second "copper value." The difference between the two values is a measure of the hydrolysis which has taken place, and is proportionate to the "degree of hydration" of the original cellulose. He gives a table of typical results. J. F. Briggs (*Papierfabrikant*, 1910, **8**, 46) regards the hydration produced by heating cellulose with water as a colloidal phenomenon of adsorption or gel formation. It is a reversible process in the sense that the water can be expelled from the solid phase by heating the fluid pulp or by treatment with alcohol. Ordinary cotton cellulose is to be regarded as a cellulose hydrate of low degree of hydration. Increased hydration, however produced, coincides with an increase in the adsorption capacity of the cellulose, *e.g.* towards metallic hydroxides, dye-stuffs, etc.

O. Miller (*Ber.*, 1910, **43**, 3430), on the other hand, states that mercerised cotton is not a cellulose hydrate. If the materials are dried at 95° C. before and after mercerisation a slight loss of weight is recorded instead of

a gain, as the result of the treatment. Then the hygroscopic moisture of mercerised cellulose is the same whether the sample be dried at 95° C. in the oven or at 25° C. over calcium chloride; a hydrate stable between these two grades of temperature is hardly conceivable. When dried *in vacuo* over sulphuric acid, mercerised cellulose has the same percentage composition as the original cellulose. The author contends that in the process of mercerisation, the sodium hydroxide enters on a state of solid solution in the cellulose, and that the process is accompanied by a partial conversion of the cellulose into an isomeride, the extent of this conversion being dependent on the concentration of the alkali: Schwalbe (*Ber.*, 1911, **44**, 151-152) combats these views of Miller, and claims that he had already proved that mercerisation is unaccompanied by the combination of water with the cellulose. The proof adduced by Miller, by weighing the cellulose before and after mercerisation, is without value, since a gain due to hydration might be neutralised by a loss due to the solubility of a portion of the cellulose in the liquid. C. F. Cross (*ibid.* 153-154) also points to the invalidity of arguments based on the absence of gain in weight as the results of mercerisation without taking into account the portion of the cellulose soluble in the alkaline lye, and affirms that an increase in weight does in fact take place. The author, in defending the application of the term "hydration" to this reaction, further argues that the water is taken up by the cellulose in definite quantitative proportions, and that this combination is accompanied by fundamental changes in the physical properties of the cellulose. The hydrates of the celluloses and their derivatives which are capable of existing between the temperatures of 0° and 50° C. are described as definite and well characterised compounds. If all these yield the same anhydrous cellulose on drying at a high temperature, this fact may be regarded as analogous to the production of the same anhydrous salt by heating the various crystal hydrates, say of sodium sulphate. Replying to the criticisms of Schwalbe and Cross, O. Miller (*Ber.*, 1911, **44**, 728) states that on mercerising cotton cellulose the mercerised product was 99·6 per cent, fibres, etc., recovered

from the lye 0·26 per cent, and loss 0·14 per cent of the original cellulose taken. The moisture of mercerised cotton is readily given off in a desiccator over calcium chloride and is not chemically fixed. The free water and water fixed in solid chemical hydrates evaporate with a constant velocity at a constant temperature under a constant tension of aqueous vapour, lower than the saturation point; but mercerised cotton was found to give up its water at by no means a constant rate, for the rate diminished rapidly over the whole period of observation.

The correctness of the view that mercerised cotton does not actually contain chemically combined water is supported by the following facts.[1] The excess of water contained in mercerised cellulose can not only be removed, and as a result the dyeing property changed, by drying (J. F. Copley, *Journ. Soc. Dyers and Col.*, 1908, **24**, 72), but also by applying heavy pressure to the fabric after mercerising and whilst in the wet state (J. Hübner, Eng. Pat. 12455), by extraction with absolute alcohol (J. Hübner and F. Teltscher, *Journ. Soc. Chem. Ind.*, 1909, **28**, 641), and by keeping the mercerised cotton for a long period in a desiccator over calcium chloride or phosphorus pentoxide (O. Miller, *loc. cit.*). It is shown on p. 81 that whereas cotton mercerised without tension took up 9·33 per cent of moisture from the air, the same cotton mercerised with tension took up only 8·28 per cent of moisture. The mercerising of the two samples was done with the same caustic soda and at the same time, and they were exposed to the same atmosphere and weighed at the same time. Samples of bleached cotton gave for cotton mercerised without tension 9·12 per cent, and with tension 8·05 per cent of moisture. Although in the one case the cotton yarn was stretched during mercerisation, the cellulose of the cotton must be in the same state as in the sample which was not stretched, for on stretching the latter it shows lustre and the properties of yarn mercerised with tension. If, therefore, it be admitted that the cellulose is the same chemical substance in the two cases, it must be admitted that the attraction of more moisture is

[1] Hübner, *Bleaching and Dyeing of Vegetable Fibrous Materials* (Constable, London, 1912).

not due to chemical difference of the cellulose in the two cases. In short, this greater affinity for moisture can only be explained by a difference of physical state. This explanation might then be taken back to the ordinary cotton, which is found to absorb less moisture than the other two varieties, and we might infer from the above reasoning that the attraction by mercerised cotton of more moisture than ordinary cotton is due not to a change in the chemical nature of the cellulose but to an alteration in its physical characteristics.

E. Knecht and W. Harrison (*Journ. Soc. Dyers and Col.*, 1912, **28**, 224) found that tetramethyl ammonium hydrate caused cotton to shrink as solutions of alkali hydroxides did. Lithium hydroxide had a greater effect than sodium or potassium hydroxides; whilst, on the other hand, calcium, barium, and ammonium hydroxide, and hydrazine hydrate produced no shrinkage.

E. Knecht (*Journ. Soc. Dyers and Col.*, 1915, **31**, 8-10) found a considerable mercerising effect is produced, without injury to the feel and tensile strength, by immersing cotton yarn for thirty seconds in hydrochloric acid of 38° Tw. Stronger acids (39°-40° Tw.) make the fibre harsh and brittle. The mercerising effect is still considerable with hydrochloric acid of 37° Tw., but ceases with weaker acids from 36° Tw. downwards; lowering the temperature does not increase the activity of the weaker acids. The mercerisation is accompanied by shrinkage amounting to 8 per cent with acid of 38° Tw. and 4 per cent with acid of 37° Tw. The yarns become curly, but attempts to produce lustre on Egyptian cotton by treatment under tension were not successful. The treated cotton exhibits most of the properties of hydrated cellulose; it is characterised by an increased affinity for substantive dye-stuffs, which is greater when the fibre is dyed without drying. The microscopic appearance is not much changed.

A number of processes have recently been patented depending on the action of sulphuric acid of various strengths on cotton. Mercer, in his original specification, mentioned the use of sulphuric acid of 10·5° Tw., but subsequent experience in mercerising showed that caustic

soda was the best agent to produce the swelling and lustring of the fibre; moreover, it could be used without risk of damaging the material. Heberlein & Co. (Eng. Pat. 100483, 1916) produce novel effects on cotton fabrics by (1) alternately treating them with alkali lye of 15° Be. and sulphuric acid of over 48° Be., and (2) submitting the cotton fabric (previously mercerised) to the action, in places, of sulphuric acid of strength greater than 50·5° Be., then washing and again mercerising. Akt. Ges. Cilander (Eng. Pat. 103432, 1916) produce transparent effects on cotton by treating with sulphuric acid of less than 50·5° Be., cooled to at least 4° C., and then mercerising with caustic soda. E. Heberlein (U.S. Pat. 1265082, 1918) produces transparent effects on cotton by subjecting the goods to the action of a caustic alkali solution of at least 15° Be., washing and then treating with sulphuric acid of at least 50·5° Be., both treatments being carried out at a temperature below 0° C.

The effect of cold during mercerisation is discussed by A. Kirchbacher (*Z. angew. Chem.*, 1910, **23**, 2269). With lyes of less than 30° B. the best results are obtained at a low temperature, but with more concentrated lyes the influence of temperature is small. He reports (*Journ. Soc. Chem. Ind.*, 1911, 20) that in Ahnert's process of mercerisation the yarns are impregnated with hot lye (25° B., sp. gr. 1·21) and then chilled. T. Nakata (*Journ. Chem. Ind.*, Tokyo, 1917, **20**, 1224-1231) states that the strength and elongation of mercerised yarns are of importance, and these properties depend on the thorough removal of the mercerising soda after mercerisation, on the amount of stretching to which the yarns are subjected during mercerisation, and on the moisture contained in the yarn before mercerisation.

In discussing the theory of the action of strong alkali hydroxides on cotton W. Harrison (*Journ. Soc. Dyers and Col.*, 1915, **31**, 198) regards mercerised cotton as containing cellulose in a higher degree of dispersion than ordinary cotton. The shrinking and untwisting of the cotton fibres during mercerisation are due to strains within the fibres acting when the cotton has been softened by the caustic soda. The lustre of mercerised fibres is attributed mainly

to their smooth surfaces in comparison with the fibres unmercerised or mercerised without tension; the section of all fibres is found to have an influence on the lustre, particularly if such fibres have smooth surfaces. He criticises Hübner and Pope's theory of lustre. The last-named authors (*Journ. Soc. Chem. Ind.*, 1904, **23**, 404-411) pointed out that the fibres untwist during the mercerising; the natural twist does not always run in the same direction, some twists being to the left and others to the right, and the untwisting during mercerisation really causes a retwisting of the fibres because the ends of the yarn are held. The lustre produced depends largely on the reflection of the light by the swollen and retwisted fibres. The mercerising agent which is able to produce a high degree of swelling, shrinking, and untwisting of the fibres therefore gives the maximum lustre. Harrison (*Proc. Roy. Soc.*, 1918, A, **94**, 460-469) regards the shrinkage of length which takes place during mercerisation as being due to the balancing of the internal stresses of the fibres (see p. 113); and regarding lustre he (Second Brit. Ass. Report on Colloid Chemistry) inclines to Lange's view that lustre is due to the smoothness of the surface of mercerised fibres as compared with ordinary cotton fibres. He maintains that the lustre of single fibres is decreased by increasing the number of twists. Regarding the twists in the natural fibres, W. L. Balls points out that when the cotton plant is 33 days old it is easy to distinguish simple pits in the cell-walls of the fibres. These pits are common in many kinds of vegetable cell-wall, and are not in any way peculiar to cotton. Given such pits, the fibre must twist when it dries, unless the wall has been thickened so much as to obliterate the central cavity almost entirely. Twisting may be left or right; the direction appears to be accidental. Further he states that lustre is probably almost synonymous with twist. If all the hairs in a sample are well and evenly twisted, there will be an infinite number of convex surfaces, each reflecting a spot of light. In addition to this there is refraction of light, which may be seen by holding a well-twisted fibre against a dull background with a good north light well overhead. It seems more than probable that the causes of lustre changes and

variations lie behind the cuticle, because the cuticle is one of the last plant tissues to be affected by ill treatment. Discussing the strength of yarns, Balls states that yarn does not break primarily through rupture of hairs, but through the slipping of hair on hair (see p. 33). Strength of yarn, within limits, follows the amount of twist which is put into it, even the variations in the strength of yarn after mercerising being accounted for in this way.

R. Haller (*Kolloid Zeits.*, 1917, **20**, 127) considers the outer membrane of vegetable fibres to be made up of two structural membranes, thus supporting Nägeli's micellary theory of the structure of vegetable membranes. The absorption of mordants and dyes by the penetration of these substances into the micellary interstices is dependent on the power of dispersion of the particles. In the case of mercerised fibres the micellae are more widely separated than in the original untreated fibres, and particles of larger size than 5 $\mu\mu$ may be absorbed, with the result that the depth of colour is greater.

As regards the different *tests for mercerised cotton* which have been suggested, it must be pointed out that in some cases, particularly in cloth mercerising, some of the fibres are not thoroughly penetrated by the caustic soda solution and some not at all. Thus Lester (*Journ. Soc. Chem. Ind.*, 1909, **28**, 230), on dyeing mercerised cotton cloth and examining it under the microscope, found that in the mercerising process the surface fibres were first acted upon, and where the time, temperature, or the strength of the soda lye is insufficient to effect complete mercerisation, the internal portions of the cloth, where the fibres are brought into closest contact, are little affected. Mercerised cotton absorbs more iodine from a potassium iodide solution than ordinary cotton does (see p. 81), and, further, it does not give up this iodine so readily to water. J. Hübner (*Journ. Soc. Chem. Ind.*, 1908, **27**, 105) has used this observation to distinguish mercerised from ordinary cotton. By dissolving 30 grms. of iodine in 100 c.c. of a saturated solution of potassium iodide in water a solution was obtained which was found to be suitable for distinguishing between mercerised and

ordinary cotton. The sample to be tested is immersed in this solution, then taken out and washed with water or with a 2 per cent solution of potassium iodide. From the manner in which the iodine is given up during the washing one can determine, after some experience of the test, whether the sample is mercerised or not, and some indication can be derived as to the strength of the caustic soda used in the mercerising. Higgins[1] has used this test in practice and found it very useful. In another test described by Hübner (*loc. cit.*) a solution of 1120 grms. of zinc chloride in 480 c.c. of water is used. To 20 c.c. of this solution one or more drops of a solution of 1 grm. of iodine and 20 grms. of potassium iodide in 100 c.c. of water are added. On putting mercerised cotton into this solution it is turned a blueish shade, whereas ordinary cotton is not similarly affected.

E. Knecht (*Journ. Soc. Dyers and Col.*, 1908, **24**, 67) found that ordinary cotton dyed with benzo-purpurine is at once turned blue by hydrochloric acid, but mercerised cotton becomes reddish-violet if the acid is not used too strong. If the solution containing the dyed cotton is heated and dilute titanous chloride (or a stronger solution of stannous chloride) be added, the colour in both cases diminishes in intensity, until just before the complete destruction of the colour takes place the ordinary cotton appears indigo blue and the mercerised cotton red. To determine the degree of mercerisation Knecht (*ibid.* 68-71) uses the selective affinity of mercerised and unmercerised cotton for dye-stuffs when dyed in the same dye-bath. After the dyeing he estimates the amount of dye-stuff in the fibre by direct titration. The results show a continuous rise in the affinity of cotton for colouring matter from untreated cotton to that mercerised with caustic soda at 70° Tw. The strength of the caustic soda which had been used for mercerising a given sample of yarn may therefore be determined by dyeing known weights of the sample and of ordinary cotton of about the same quality in the same bath. The colour is then estimated quantitatively in both samples, and from the results the degree of mercerisation can be arrived at by

[1] *The Dyeing Industry* (Manchester University Press).

using a table given. A. B. Knaggs (*Journ. Soc. Dyers and Col.*, 1908, **24**, 112-113) states that the addition of titanous chloride in the above test (Knecht's) is not necessary, the colour changes being produced by the hydrochloric acid alone. Oxycellulose behaves in a somewhat similar manner to mercerised cotton, but the colour produced is blue-black instead of blueish-violet.

Photo-micrographs of mercerised cotton cloth were found by J. Hübner (*Journ. Soc. Dyers and Col.*, 1911, **27**, 128) to show the cloth was more open after mercerisation under tension and that the material loses considerably in thickness.

E. Justin-Mueller (*Journ. Soc. Dyers and Col.*, 1914, **30**, 354) described a machine to measure the degree of swelling of threads, the method being useful for determining the most suitable concentration of caustic soda and time of immersion for mercerising cotton.

CHAPTER XI

CELLULOSE AND ACIDS

Effect of strong and weak acids—Tests for acid in cloth—Magnesium chloride in singeing—Hydrocellulose—Tests for hydrocellulose.

A NUMBER of papers of great interest to bleachers have recently appeared, dealing with the action of different acids on cotton. H. Wilkinson (*Journ. Soc. Dyers and Col.*, 1917, **33**, 148) finds the tendering action of sulphuric acid increases the longer the acid is in contact with the fibre, and on washing with water or alkali the cotton regains in strength an amount approximately equal to the strength in the acidified condition. The acid-treated cotton behaved like ordinary cotton on mercerising, that is, it gained further in strength. W. Harrison (*Journ. Soc. Dyers and Col.*, 1912, **28**, 238) found dilute sulphuric acid dried on cotton causes it to take up more methylene blue and less of direct dye-stuffs, this property being usually regarded as characteristic of oxycellulose. The product formed by the action of the sulphuric acid is not oxycellulose nor a sulphuric ester of cellulose, but is most probably a colloidal form of hydrocellulose. G. E. Pilkington (*Journ. Soc. Dyers and Col.*, 1915, **31**, 149-153) states that oxalic, tartaric, and citric acids have a tendering action on cotton, the first-named being the most active in this respect. The effect was measured by a determination of the "copper values" in the different actions. Sodium sulphate diminished the action of these acids. M. Cohen (*Journ. Soc. Dyers and Col.*, 1915, **31**, 162), on boiling cotton for one hour with hydrochloric acid of $\frac{1}{128}$ per cent and upwards, found that the "copper value" of the cotton

was in all cases increased, whereas sulphuric acid produced no appreciable effect if the concentration was less than $\frac{1}{32}$ per cent. If the cotton is soaked in cold acid, dried, and then heated to 120° C. for ten minutes, an acid of as low a strength as $\frac{1}{400}$ per cent in the case of hydrochloric acid and of $\frac{1}{128}$ per cent in the case of sulphuric acid was found to be effective, owing to the concentration of the acid on the fibre. The increase in the "copper value" corresponded with the decrease in the tensile strength of the yarns. C. G. Schwalbe and M. Robinoff (*Z. angew. Chem.*, 1911, **24**, 256), using Egyptian cotton of copper value 0·04, found, on bleaching with hypochlorite solutions and souring by hydrochloric or acetic acid, that the formation of hydrocellulose was promoted by the use of lower strengths of acid. The results were confirmed by noticing the solubility of the cellulose produced in dilute lyes. Robinoff further supports this statement in a later paper (*Papierfabrikant*, 1912, **10**, 968), saying that dilute acids, used for souring after bleaching, act more strongly on the cellulose than acid of double or four times the strength. Acetic acid was said to apparently have as great an action as hydrochloric acid.

A. Leighton (*Journ. Phys. Chem.*, 1916, **20**, 188) finds that hydrochloric, sulphuric, and phosphoric acids do not form compounds with cotton at ordinary temperatures. Cellulose adsorbs sulphuric acid more than phosphoric acid, and the latter acid more than hydrochloric acid, whilst the presence of any of these acids reduces the amount of water which can be absorbed by the cotton. Selective adsorption was only pronounced at high concentrations of the acids; it does not occur with phosphoric acid, and is more pronounced with hydrochloric than with sulphuric acid.

To test for free acid in cloth, J. F. Briggs (*Journ. Soc. Chem. Ind.*, 1916, **35**, 80) uses potassium iodide-iodate and starch. This is made up with distilled water and adjusted for neutrality by the addition of a drop or two of N/10 acid until the liquor shows a light blue colour. The indications of this test have a roughly quantitative significance depending on the time required to develop a blueish stain. This appears at once in the presence of an objectionable

amount of free acid; if no signs of a stain are visible within five minutes the cloth may be regarded as safely neutral. Putting the cloth under a hot iron and noticing if any tendering effect is produced is regarded by J. H. Lester (*Journ. Soc. Chem. Ind.*, 1915, **34**, 934) as a better practical test than quantitative tests for acids present in the cloth. Tendering due to acids depends on the care taken in drying and on the amount of moisture left in the cloth; but no cloth should contain as much as 0·1 per cent of acid. The maximum allowable would appear to be 0·01 per cent. Briggs (*loc. cit.*), in discussing the hot-iron test, points out that chlorides, such as calcium chlorides used in finishing embroidered goods, will also cause tendering. The effect of chlorides in white finished goods is to make them feel fuller and heavier in the hand, and the present author finds that the presence of these chlorides is sometimes difficult to detect, because many materials used in finishing are apt to contain small amounts of chlorides as impurities. In one case, goods became tender under the iron, but no acid was noticeable; calcium chloride was, however, found to be present. Under the iron, the heat decomposed the chloride, liberating hydrochloric acid; but as the cloth cooled down, after the release of the iron, the acid recombined with the lime and could not be detected.

The above facts are of interest in connection with the tendering caused by chlorides in the singeing process. F. Whowell (*Textile Inst. Journ.*, 1911, **2**, 43-53) points out that the sizer frequently incorporates a small amount of zinc chloride with his size, which acts as an antiseptic, preventing mildew, and also as a deliquescent. Other chlorides are also frequently employed as deliquescent agents, *e.g.* those of magnesium and calcium. All these chlorides tend to dissociate when heated above a certain temperature, and cloths containing them are liable to become tendered after passing through the singeing process. The heat of the singeing machine liberates hydrochloric acid, which destroys the fibres of the cloth. The damaged parts are often irregularly distributed over the cloth, and they show themselves in the form of small or large holes with clean-cut edges, distinct from the frayed edges of

mechanically damaged parts. Sometimes chlorides are also used for weighting grey cloth, the cloth being thus enabled to carry more filling. Donninelli (*Rev. Gen. Mat. Col.*, 1908, **12**, 203-204) also points to the effect of magnesium chloride during singeing, a loss of strength of 53 per cent on the warp and only 28 per cent on the weft being noticed after singeing, dyeing, and schreinering. Merchants are recommended to insist that the size used for the warps shall be free from magnesium chloride. Paper containing magnesium chloride was practically destroyed on heating for thirty days at 60° C., but storage for four years at ordinary temperatures had little effect on the strength (C. Bartsch, *Mitt. K. Materialprüf*, 1913, **30**, 400).

T. W. Fox, J. Hübner, and E. Knecht (*Text. Inst. Journ.*, 1912, **3**, 27-42) found magnesium chloride to be stable at 100° C., to decompose slightly at 120° C. and rapidly at 149° C. On singeing cotton cloth containing magnesium chloride, no appreciable tendering of the cloth was found after one or two singeings, so breaking tests were confined to cotton thrice singed, then boiled in caustic soda lye under pressure. The results given below show that other substances used in sizing, besides magnesium chloride, produce tendering, and sometimes in quite as marked a degree :

Salt used.	Percentage Loss after thrice singeing.	Percentage Loss after subsequent boiling.	Total Loss of Strength.
Ammonium chloride .	5·5	26·0	31·5
Calcium chloride . .	11·0	10·0	21·0
Magnesium chloride .	6·0	17·0	23·0
Sodium chloride . .	12·5	10·0	22·5
Zinc chloride . . .	3·0	29·0	26·0
Glucose	no change	13·0	13·0
Salicylic acid . . .	8·0	17·0	25·0
Carbolic acid . . .	1·0	19·0	20·0
Aluminium chloride .	22·0	23·0	45·0
Sour size . . .	8·0	18·0	26·0
Unsized cloth . . .	...	17·0	17·0

W. Thomson (*Journ. Soc. Dyers and Col.*, 1915, **31**, 133) found that whereas 5 per cent solutions of magnesium

and zinc chlorides both caused charring of cloth on ironing (the latter at a lower temperature), a mixture of the two solutions only caused at the most a slight discoloration. He had also noticed a similar result in singeing operations. A double chloride might be formed, but attempts to isolate this were not successful. The mixed chlorides are used in practice, the zinc chloride being added to act as an antiseptic. M. Fort and M. Pickles (*Journ. Soc. Dyers and Col.*, 1915, **31**, 255) showed that on adding sodium chloride to magnesium chloride the tendering action of the latter was reduced, because the introduction of a salt containing a similar ion into a solution of an acid lowers the electrolytic dissociation of the acid and causes a corresponding reduction in its tendering action. E. Ristenpart (*Z. angew. Chem.*, 1912, **25**, 289) observed that magnesium chloride does not suffer decomposition below 106° C., and, even when heated to 246° C., the free hydrochloric acid formed is only equal to about 2 per cent of the weight of the salt taken. Tendering, therefore, cannot take place below 106° C. ; but at higher temperatures, especially if long continued, the goods become tendered. Goods containing magnesium chloride cannot be dried with safety above 100° C. A. Leighton (*loc. cit.*) found when cotton is treated with small quantities of sulphuric acid, *e.g.* 0·01-0·02 per cent, and dried at a low temperature, its strength is not decreased, but even increased.

Pure cotton cellulose on putting into weak acids and alkalis was found by Mills to react, some of the acid and alkali being absorbed, and Vignon found that heat was produced during the absorption. Cellulose has therefore weak acidic and basic properties, but these values are found to be practically insignificant.

Stern (*Journ. Chem. Soc.*, 1904, **85**, 336) states that under the action of hot dilute acids cellulose does not produce **hydrocellulose**, as stated by Girard (*Compt. Rend.*, **81**, 1105 ; **88**, 1322). The cellulose is partly hydrolysed with the production of soluble products, probably d. glucose. The residue does not differ in elementary composition from the original cellulose, and its disintegration is due to the fact that certain portions of the fibre are

more easily attacked than others: as a result of their solution and removal the whole fibre falls to pieces. Cross and Bevan (*Journ. Chem. Soc.*, 1904), on the other hand, contend that the residues are different from the original cellulose in that they are attacked by alkaline solutions, being largely soluble in 15 to 20 per cent caustic soda solution, are oxidised by Fehling's solution, and generally show differences in the reactivity of the typical carbonyl and hydroxyl groups. Their behaviour towards nitric acid, acetic anhydride, and esterifying agents generally differs from that of the original cellulose, and the properties of the corresponding derivatives are also different.

O. Hauser and H. Herzfeld (*Chem.-Zeit.*, 1915, **39**, 689) state hydrocellulose is differentiated from cellulose by its cupric-reducing properties, ready solubility in cellulose solvents, low hygroscopic moisture, and blue reaction with iodine-potassium iodide, which is quickly removed by water. It is probably an adsorption compound of variable composition, consisting of cellulose in combination with its products of hydrolysis, including dextrose and most probably various dextrins. The brittle nature is partly attributed to the interpenetration of the cellulose structure by gelatinised products of hydrolysis. On extracting with water in a Soxhlet's apparatus the first extracts had a high cupric reducing value, whereas finally a residue was obtained, the copper value of which was low. G. Büttner and J. Neumann (*Z. angew. Chem.*, 1908, **21**, 2609) describe hydrocellulose as a white sandy powder, extremely resistant towards acids and alkalis, but C. G. Schwalbe (*Z. angew. Chem.*, 1909, **22**, 155-156) combats this statement, for as much as 52 per cent of Girard's hydrocellulose is dissolved by boiling with a 15 per cent solution of sodium hydroxide solution. H. Jentgen (*Z. angew. Chem.*, 1910, **23**, 1541) also states that hydrocellulose is largely soluble in caustic soda. He states that about $\frac{1}{3}$ is so dissolved, and of this 85 per cent is reprecipitated from the soda on adding acid, the remainder being more or less soluble and profoundly decomposed. Several salts of strong acids with weak bases also convert cellulose into hydrocellulose, the action of these salts being direct

and not depending on dissociation. In the production of hydrocellulose by acids the acid enters into association with the cellulose by adsorption, and the hydrolysis proceeds by the action of the finely divided water on the adsorption compound, the acid acting as a contact agent. He later states (*Z. angew. Chem.*, 1911, **24**, 11-12) that (1) 1 per cent aqueous solutions of acid have practically no action on cellulose; (2) alcoholic solutions of acids hydrolyse only very slowly, and the rate of hydrolysis is directly influenced by the dissociating capacity of the solvent; and (3) 1 per cent solutions of acids in non-dissociating solvents hydrolyse cellulose rapidly. He maintains that these observations support his previously expressed views, but Schwalbe (*ibid.* 12-13) holds that dilute aqueous acids do have a hydrolysing action on cellulose and that the hydrolysing power of alcoholic solutions of acid is reduced because the acid tends to form esters with the alcohol.

H. Ost discusses the absorption of moisture by hydrocellulose (see p. 82), and W. O. Coninck (*Chem. Zentr.*, 1910, **2**, 1459) finds that filter paper subjected to the action of concentrated hydrochloric acid for 62 hours does not yield a product which reduces Fehling's solution, but by the action of concentrated hydrochloric acid for 87 hours and of fuming hydrobromic acid for 24 hours such a product is obtained from cotton.

As far as the bleacher is concerned, it must be admitted that this subject of the existence or non-existence of a definite substance, hydrocellulose, is not yet sufficiently developed to give him any definite information. In fact, out of the researches no definite means of detecting hydrocellulose and distinguishing it from oxycellulose can be gathered. It is stated that hydrocellulose shows the same reaction with Fehling's solution and caustic soda as oxycellulose, but it does not show the methylene blue test. As pointed out by J. F. Briggs (*Journ. Soc. Chem. Ind.*, 1916, **35**, 80), however, the value of this negative distinction is limited to cases of local tendering since the dyeing test is not available in cases of general tendering. Even the methylene blue test is further discounted by the observation of M. Freiberger (*Z. angew. Chem.*, 1916, **29**,

397) that cotton after souring takes up more methylene blue than the unsoured material.

R. Haller (*Kolloid. Zeits.*, 1917, 20, 127) states that the chemical and physical properties of cotton fibres lead to the conclusion that the outer membrane consists of two structural elements which show but small differences under normal conditions. When the cellulose is transformed into hydrocellulose and oxycellulose the two components are much more readily differentiated. The difference is shown in the behaviour towards chemical reagents and in the appearance under the ultramicroscope.

CHAPTER XII

CELLULOSE AND OXIDISING AGENTS

Oxycellulose—Tests for oxycellulose—Action of ozone on cellulose—Action of metallic oxides.

In cases of over-bleaching, that is, after the hypochlorite or other oxidising agent has acted on and destroyed the colouring matter of the fibre, the cellulose is attacked. This action results in the cellulose becoming changed in its power of resisting the action of alkalis, in its increased reducing action on Fehling's solution, and in its increased power of adsorbing methylene blue from solution. The cellulose is said to be changed to oxycellulose, and, since the discovery of this substance or collection of substances by Witz, this action has been a subject of controversy among chemists. As in the case of hydrocellulose, there are no definitely accepted opinions as to its nature, and as previously stated no means have yet been devised for definitely distinguishing this cellulose product from the other product generally known as hydrocellulose. Faber and Tollens found on distillation with weak acid it yielded furfural, and by boiling with lime iso-saccharic acid and dioxybutyric acid. They contend (*Ber.*, 1899, 2589) that oxycelluloses are mixtures of cellulose and a derivative oxidised compound, which contains one more atom of oxygen than cellulose. L. Vignon (*Bull. Soc. Chim.*, 1901, 325 and 130) digested various celluloses with dilute hydrochloric acid for six hours at 100° C., and estimated the cupric reduction of the soluble products calculated as dextrose.

100 grms.	Equal to dextrose grms.
Purified cotton	3·29
„ hydrocellulose	9·70
Cotton mercerised (NaOH 30° B.)	4·39
„ „ („ 40° B.)	3·51
Cellulose precipitated from cuprammonium	4·39
Oxycellulose	14·70
Starch	98·6

W. O. Bancroft and R. H. Currie, jun. (*Journ. Phys. Chem.*, 1915, **19**, 159-168), regard oxycellulose as always being the same product whether prepared by the action of nitric acid, permanganate, chloric acid, bleaching powder or bleaching powder and air. The authors did not succeed in converting the whole of the cellulose into oxycellulose, and it is doubtful whether pure oxycellulose has ever been prepared. Oxycellulose is partially soluble in dilute alkali hydroxides, with a yellow colour on heating; the residue is simply unoxidised cellulose in varying proportions. The dissolved substance is precipitated by alcohol and acids, and after dialysis it is readily soluble in water. This soluble substance is regarded as the true oxycellulose and may be a homogeneous substance. The distinction made by Nastjukoff between α, β, and γ oxycelluloses does not exist. The so-called α oxycellulose is unattacked cellulose, more or less contaminated with products of decomposition; β (alkali-soluble) and γ (water-soluble) oxycelluloses are the same substance in different states of aggregation. The cupric-reducing property of oxycellulose is probably not characteristic and may be due to the presence of other decomposition products; this property readily disappears on prolonged heating without any essential change in the other characteristics of the oxycellulose.

W. Harrison (*Jour. Soc. Dyers and Col.*, 1912, **28**, 359) regards the evidence available to indicate that the different forms of oxycellulose and hydrocellulose are adsorption compounds of cellulose and its product of hydrolysis. These adsorbed reducing substances are probably of an aldehydic nature in hydrocellulose and of an acidic nature in oxycellulose. R. Oertel (*Z.*

angew. Chem., 1913, **26**, 246) found oxycellulose to have a furfural value of 1·7 against that of ordinary cotton of less than 1, but he contends that the furfural value is not sufficiently definite to serve for the characterisation of oxycellulose. Oxycellulose is stated to be an oxidised derivative of hydrocellulose, not a homogeneous product. Ditz (*Journ. Prakt. Chem.*, 1908, **78**, 343-364) states that oxycellulose placed in Nessler's solution at ordinary temperatures is coloured brown at first, but rapidly assumes a dark grey shade due to the reduction of the mercury salt. He proposes this as a test for oxycellulose, since cellulose and hydrocellulose do not react in this way except they contain some oxycellulose. G. Kita (*Journ. Chem. Ind.*, Tokyo, 1917, **20**, 138) finds that methylene blue cannot be used to estimate oxycellulose, because there is no proportionality between the quantity of methylene blue absorbed and the quantity of oxycellulose present. R. Scholl and W. F. A. Ermen estimate oxycellulose by its action in reducing vat dye-stuffs (p. 43).

C. Dorée (*Journ. Soc. Dyers and Col.*, 1913, **29**, 205) found, on exposing cotton to ozone, the "copper value" of ordinary and mercerised cotton increased from 1·2 to 16·9 and 1·7 to 24·0 respectively. The loss in weight in subsequent boiling with potassium hydroxide was 64 and 57 per cent respectively. L. L. Lloyd (*Journ. Soc. Dyers and Col.*, 1910, **26**, 273) finds that material showing 5 per cent decrease in strength due to overbleaching will show a faint pink stain with Fehling's solution. Oxycellulose is formed by the action of many metallic salts on moist cotton at 50° C. The amount produced depends on the time and temperature of ageing and on the amount and nature of the metallic salts present. The metals, the salts of which act in this case as catalysts, are, in order of their activity, copper, cobalt, manganese, nickel, iron, and to a small extent chromium. Their most active salts are nitrates, then chlorides, and finally sulphates. The oxycellulose produced may be reduced by various agents, but the tendering remains unaltered. The production of oxycellulose is also mentioned on p. 128. The metals mentioned by Lloyd and in the order of activity given are

those which cause the tendering of cotton and linen in the presence of hypochlorites and peroxides (see p. 57).

As regards the action of different oxidising solutions, used for bleaching, on the cellulose itself, H. Moore (*Journ. Soc. Dyers and Col.*, 1915, **31**, 180) found that the effect of the moderate addition of acid to hypochlorite solutions was to decrease the amount of the oxycellulose formed during the bleaching of cotton and not to increase it. On the addition of alkali to the bleach a minimum amount of oxycellulose was formed at a certain concentration of the alkali. Permanganate solutions gave similar results.

J. F. Briggs (*Journ. Soc. Chem. Ind.*, 1916, **35**, 78) points out that sometimes there is a difficulty in carrying out the usual tests for oxycellulose. If goods are over-chemiced at the beginning of the bleaching process, the subsequent treatment with alkaline liquors eliminates the oxycellulose to a large extent. Moreover, the non-cellulose constituents of vegetable fibres oxidise to compounds comparable with oxycellulose.

CHAPTER XIII

CELLULOSE—THE BLEACHED PRODUCT

Degree of bleaching of cellulose—Copper value of cellulose—Copper sulphate value — Standardisation of bleached whites — Changes in cellulose during bleaching—Strength of finished goods—Action of light on cotton—Strength of cotton fibres—Absorption of salts by cotton from solutions.

VARIOUS methods of determining the *degree of bleaching* have been proposed. C. G. Schwalbe (*Färber-Zeit.*, 1908, **19**, 33-34) describes the following method. A weighed quantity of the cotton is boiled with a measured quantity of Fehling's solution, the solution being well stirred before reduction. The copper separated is filtered off, washed with hot water, dissolved in nitric acid, and estimated by electrolytic deposition. The electrolysis is carried out in a platinum bowl, using a revolving anode. In this way the "copper value" for the sample of cotton is obtained. Different varieties of cotton give different figures, and those for mercerised cotton are higher than for ordinary cotton. The moisture in the sample is determined by using a toluol drying stove. Later, Schwalbe (*Z. angew. Chem.*, 1914, **27**, 567) states that in the determination of the cupric-reducing value of cellulose the limits of variation between duplicate tests should not exceed 0·2 in the "copper value," but abnormal results, *e.g.* values ranging from 0·6 to 1·3, may be obtained through the presence of cupric-reducing impurities in the Rochelle salt or the water employed. The solutions used should always be controlled by a blank test, during which the liquid should neither turn greenish in colour nor deposit a precipitate of cuprous oxide on standing. M. Freiberger (*Z. angew. Chem.*, 1917,

30, 121) also points to precautions required in this determination. The chemicals used must be carefully purified; the boiling should be carefully controlled; and a blank determination should be made in which only a slight quantity of copper should separate.

Schwalbe (*Z. angew. Chem.*, 1910, **23**, 924-928) criticises Vieweg's proposal (*Papier-Zeit.*, 1909, **34**, 149) to measure the degree of damage suffered by cellulose in bleaching, by determining the proportion of sodium hydroxide it neutralises on boiling for 15 minutes in a 1 per cent solution. He shows that the decomposition of oxycellulose, hydrocellulose, and cellulose itself by boiling alkali does not reach a final point; also mercerised cotton shows a smaller consumption of alkali than the original cellulose.

The attraction of cellulose for neutral salts is used by B. Rassow (*Z. angew. Chem.*, 1911, **24**, 1127) as a method of distinguishing celluloses. Cotton cellulose absorbs and fixes small amounts of copper from copper solutions, and the copper cannot be removed by washing. Unbleached cotton absorbs more copper than bleached, whereas, if the cotton be thoroughly purified its absorption is slight. The author suggests a "copper sulphate value" for celluloses. C. Piest (*Z. angew. Chem.*, 1912, **25**, 2518) states that the "copper value" standardised by Schwalbe is the most definite measure available for the diagnosis of chemical modification in celluloses, particularly by over-bleaching. Normally purified cottons show a total "copper value" considerably below 2 and preferably not exceeding 1, whereas the copper value of strongly over-bleached cottons may rise as high as 16. Hydrocellulose also shows an increased "copper value," but in a minor degree. The "copper sulphate value" shows differences too small for practical use. E. Sutermeister (*Papierfab.*, 1914, **12**, 898) found on examining bleached pulp (*a*) by "copper value" and (*b*) by loss on boiling with 0·25 per cent caustic soda that parallel results were obtained.

Cross and Bevan (*Researches on Cellulose*, 1905-1910) give the following figures for samples of bleached cotton cloth:

Kind of Cloth.	Solubility in 3 per cent NaOH.	Copper Value.	Ash per cent.
Madder bleached	3·41	0·45	0·096
„ afterwards "malted" .	3·14	0·43	0·098
„ reboiled in alkali . .	1·66	0·39	0·150
Mercerised grey and then bleached without lime	4·23	0·54	0·110
„ afterwards "malted" .	2·39	0·35	0·090

M. Freiberger (*Färber-Zeit.*, 1915, **26**, 319; 1916, **27**, 26) attempts to standardise the whites of bleached cotton cloth by noticing the stains produced on the samples of cloth by waste bowking liquors diluted to known strengths. The samples were then dried. A range of standards from pure white to grey unbleached material was obtained in this way, by means of which it was easy to distinguish a difference of 5 per cent in the extent of bleaching. R. Haller (*Färber-Zeit.*, 1916, **27**, 6) criticises this suggested method, stating that it is only applicable if the same system of bleaching and the same system of bowking have been used as were used in the preparation of the standards. This criticism is justified in the light of information previously given regarding the removal of the non-cellulose impurities by different systems of scouring, and it has been pointed out that if different qualities and weaves of cloth are used distinction will be difficult.[1]

Opinions vary as to the changes which take place in fibres during the bleaching process. Minajeff (*Z. Farben-Ind.*, 1908, 7, 1-3, 7-21) finds the cuticle is not absent from mercerised and well-bleached cotton, as has been stated by C. O'Neill. The cuticle contains a substance called *cutin*, which is encrusted with fats, waxes, and colouring matter in the raw fibre. It is insoluble in sulphuric acid. Alkaline boiling removes the incrustants, but does not affect the cutin. In some cases it is difficult to distinguish the cuticle under the microscope, and the different mechanical and chemical treatments increase the difficulties of distinguishing. The cuticle resists the action

[1] Higgins, *Annual Reports on Applied Chemistry*, 1917.

of cuprammonium solution, fairly strong sulphuric acid, boiling alkaline liquids, and mercerising soda: in the bleached fibre it has the same properties as in the unbleached fibre, although these are not so easily distinguished. By the microscopic examination of cotton and linen under high powers E. Seel and A. Sander (*Z. angew. Chem.*, 1916, **29**, 261) found no structural modification in fibres treated with acids, alkalis, or oxidising agents (compare Robinoff, pp. 80 and 99).

W. Harrison (*Proc. Roy. Soc.*, 1918, A, **94**, 460-469) found double refraction in textile fibres due to the presence of internal stresses, and it may be increased by compressing the fibres. After the removal of the pressure the fibres did not return to their original shape, and the increased double refraction of the compressed portion remained until the stresses were relieved by immersion in water. Fibres subjected to a limited amount of extension when dry do not return to their original length when kept loose in a dry atmosphere, but do so rapidly when placed in water; the effect of a humid atmosphere is the same as that of cold water but much less rapid. At high temperatures water renders fibres truly plastic; deformation is produced by compression, but little or no internal stresses result. A modification of the internal stresses takes place when fibres are boiled with alkalis, and the shrinkage in length which takes place during mercerisation is due to the balancing of the internal stresses.

It has been stated (*Chem. Zeit.*, 1915, **39**, 62) that on removing the dressing from bleached linen and cotton goods there is no noticeable difference in strength produced, but the elongation before rupture was in general greater after the removal. E. Ruf (*Z. ges. Textil-Ind.*, 1915, **18**, 202) found that goods heavily filled with magnesium sulphate were apparently very tender and did not resist the slightest strain, but on washing the original strength was restored.

Grassing, that is, exposing to air and light by spreading on the grass, is still practised for the bleaching of linen goods, and it is known that sometimes goods are tendered during this treatment. The action of light on cotton has been studied by A. Scheurer (*Bull. Soc. Ind. Mulhouse*,

1910, **80**, 324-331). A sample of white cotton was covered in places with thin glass and exposed to the radiations of a quartz-mercury lamp for 48 to 144 hours. It became yellow in colour, and a deeper yellow as the period of exposure increased. The fabric was tendered at the exposed parts; it dyed a blue shade with methylene blue and reduced Fehling's solution at these parts. A covering of quartz had no effect in preventing the yellowing, but thick glass completely stopped the action. C. Dorée and J. W. W. Dyer (*Journ. Soc. Dyers and Col.*, 1917, **33**, 17-19) supported Scheurer's observation that the light of the Cooper-Hewitt lamp turned cotton to oxycellulose. They considered this might be due to the development of ozone, which is known to convert cellulose into acidic, alkali-soluble products having the properties of oxycellulose. C. Dorée (*Journ. Soc. Dyers and Col.*, 1913, **29**, 205) extracted cotton yarns with alcohol, ether, and water, and exposed them to ozonised oxygen (1·5-2 per cent ozone). A decrease in strength of as much as 50 per cent in twelve hours was found. Flax was also rapidly attacked, solid acids and formic acid being formed.

R. S. Greenwood (*Textile Inst. Journ.*, 1919, **10**, 275) investigated the effect of the bleaching process on single fibres of cotton, the fibres being held in position by two pieces of paper and broken in a testing machine. It was found that single cotton fibres actually decreased 20 per cent in strength during the bleaching process, although cotton yarn actually increased in strength, as previously explained. Mercerisation did not increase the strengths of the individual fibres, although this process did strengthen cotton yarn. Whether the single fibres were allowed to shrink or left stretched they did not increase in strength, and this observation pointed to the conclusion that the increase in strength of cotton yarns during mercerisation was due to a physical change in the association of the fibres. Cotton at different stages of the bleaching process has been found to show a variable negative absorption for aluminium acetate from solution (R. Haller, *Chem. Zeit.*, 1918, **42**, 597-599). This negative absorption decreases as the degree of purification of the cotton increases. Cotton boiled with lime gave higher results than cotton

boiled with caustic soda. Negative absorption was most pronounced in the case of Egyptian cotton. Using aluminium sulphate solution, positive absorption was observed in all cases with raw cottons and those which had been lime-boiled; on the other hand, the well-scoured and fully bleached samples all showed negative absorption increasing generally with the degree of purification. Lead acetate showed in all cases a large positive absorption, increasing with the degree of purification. Maximum absorption in all cases seemed to correspond with maximum purification of the cotton; but treatment with bleaching liquor appears to decrease the purity of the cellulose; at any rate, it lowers the absorption values. G. Durst (*Chem. Zeit.*, 1919, **43**, 374-375) states that bleached cotton immersed in a solution of aluminium acetate for 24 hours absorbs about 0·1 per cent of alumina, half of which is fixed on the cotton.

CHAPTER XIV

VEGETABLE FIBRES AND FERMENTATION

Enzymes—Use for removing starch—Use as bleaching agents—Bacterial deterioration of cotton during storage.

The process of fermentation was first observed in the case of the yeast plant, but later it was found to be a most common process in nature : enzymes, or soluble ferments, which cause this action, were found to be secreted by plant cells. The action of these enzymes is not at all completely understood, for without appearing to enter into the composition of the substances which are formed by their activity, they carry out a large amount of work without being used up. They work best in the dark. Pasteur introduced pure cultures, and thus greatly assisted this branch of the subject.

As regards textile fibres being treated to separate their non-cellulose constituents, we have to deal with waxes, proteins, colouring matters, and carbohydrates, and it has been found that in nature the work of particular enzymes is to decompose these substances. Thus, the enzymes which decompose fats are known as lipases, but whether there are many different kinds of these is not known. The decomposition of fats by these agents has not yet been fully investigated, but the action is generally accompanied by the appearance of starch grains. The lipase first splits the fat up into glycerine and free fatty acid, but the subsequent decompositions are very complex, among the products being lecithin and simpler fatty bodies. Proteoclastic enzymes—*e.g.* peptase, tryptase, ereptase—act on proteins, converting them to peptones and amino-acids, probably by a process of hydrolysis. In the absence of air,

proteins are also broken down by certain bacteria, putrefaction being caused and evil-smelling products being evolved; but in the presence of air these substances disappear. The protein molecules, after passing through numerous intermediate stages, are finally broken down to a few simple bodies, viz. carbon dioxide, methane, hydrogen, ammonia, nitrogen, hydrogen sulphide, and phosphoric acid. Oxidases are widely distributed, and are concerned in bringing about the presence of particular colouring matters; reductases are enzymes of a similar character acting in an opposite manner. A number of enzymes—*e.g.* zymase, diastase, invertase—act on carbohydrates, and cytase hydrolyses cellulose. Cytase occurs in various seeds, and dissolves the wall of the endosperm, the process of decomposition of the cellulose being very slow. Cytase exists in some fungi and in certain bacteria. Omelianski (*Centralbl. Bakt.*, 1902, **11**, 8, 193) decomposed cellulose by fermentation into acetic acid, butyric acid, traces of other fatty acids, carbon dioxide, and water. By the aid of another bacillus he obtained methane from cellulose. Winogradsgy, also using butyric acid bacteria, showed that pectins were dissolved out by fermentation. Then we know that pectase, an enzyme, forms vegetable jelly from pectic substances existing in the cell wall.

G. P. Koch (*Soil Sci.*, 1918, **5**, 219-224) found that potassium was necessary for the development and activity of *B. subtilis*. This is also the case in plant growth, and the presence of this element and others may be essential in fermentation processes for treating textile fibres. It has also been found that soil organisms appear by preference to attack carbohydrates, and as long as they can get these, they make little attempt to break down proteins.

B. S. Levine (*Journ. Ind. Eng. Chem.*, 1916, **8**, 298), from laboratory experiments with different species of bacteria (*Bac. amylolyticus*, *Bac. fimi*, *Bac. bibulus*, *Bac. carotovorus*, and *Bac. subtilis*, Ehrenberg) in a nutrient solution containing 1 grm. each of dipotassium phosphate and magnesium sulphate, and 2 grms. each of sodium chloride, ammonium sulphate, and calcium hydroxide per litre, showed that the nitrogenous substances and ether soluble impurities of cotton can be

efficiently removed by bacterial action. The bacteria mentioned converted starch sizing only to dextrins, and had little action on the alcohol soluble impurities. On the large scale the materials are incubated with the bacteria culture for periods ranging from 72 down to 24 hours. O. Röhm (Eng. Pat. 100, 224, 1916) protects the following process. The treatment of raw cotton with boiling alkalis, preparatory to bleaching, is omitted, and the material is softened by steeping in a 0·1 per cent aqueous solution of pancreatin at 20°-40° C. for some hours. It is then bleached by the usual agents. Other enzymes, such as papayotin, ricinus enzymes, etc., may be used instead of the commercial enzyme.

Higgins,[1] in discussing these processes, states that the use of enzymes in the bleaching of cotton is of interest; previously they had been used extensively to remove the size from cotton cloth before scouring, but in this new development the action of the enzyme is to remove the fatty matters and the proteins from the fibre besides the dressing. The following questions, however, arise: (1) Can all the impurities be removed without resorting to ordinary scouring? (2) How does the cost of the nutrient solution compare with that of ordinary scouring solutions? (3) If lime salts are used in the nutrient solution, is it necessary to treat with acid after the action of the enzymes in order to get rid of the lime? As previously mentioned, some enzymes attack cellulose, and this action must be prevented, or the method of cleaning may have an effect on the strength of the fibre, just as over-retting rots linen. It might be difficult to stop the action when the non-cellulose constituents of the fibres have been removed and the cellulose itself not attacked. It must not be forgotten that caustic soda boiling has no deleterious effect on cotton and that it is an ideal scouring agent; it saponifies the waxes, hydrolyses the proteins, and eliminates the pectic matters of the fibres. Perhaps the most important point in bleaching is safety, and it is this point that these new methods will have to satisfy.

A. Bordin and J. Effront (Eng. Pat. 1411, 1915) remove the dressing from textile fabrics by the action of bacterial

[1] *Annual Reports on Progress in Applied Chemistry*, 1917.

diastases from the species *subtilis* and *mesentericus* in the presence of a small amount of a suitable alkali. The diastases may be prepared from soya cake.

E. Justin Mueller (*Bull. Soc. Ind. Mulhouse*, 1909, **79**, 21), as a result of a comparison of the material turned out from a number of bleachworks, concludes that the most important factor in the removal of the dressing is the duration of the lye boil. Different methods of bleaching, properly carried out, yield almost equally good results. An acid steep in dilute sulphuric or hydrochloric acid does not appear to be very efficacious, and the most efficient and rapid agent for the destruction of the starch is diastafor.

In the retting of flax, a particular organism, *Bacillus amylobacter*, has been isolated, and is stated to be the active agent in pectin fermentation. This organism is said to have no action on cellulose. By adding salts to the retting water, which assist the growth of the organism, the time of retting can be considerably reduced. G. Rossi (*Bull. Agric. Intell.*, 1916, **8**, 1067) uses pure cultures of specific pectic bacteria, particularly *B. comesii*, in water solutions at 28°-35° C. to remove the pectic matter from flax, that is, to ret it. He aerates during the process to prevent the development of foreign organisms which will be inimical to the cellulose. The bacteria mentioned have no effect on the cellulose, and, although they eliminate the pectic matter, they have apparently no effect on the other non-cellulose constituents of the fibre.

N. Fleming and A. C. Thaysen (*Biochem. Journ.*, 1919, 329) describe observations on the bacterial deterioration of damp cotton during storage. They find that this action ceases when the proportion of moisture falls to less than 9 per cent. If cotton is completely sterilised it can be stored wet without decomposition. The infection of cotton with bacteria is unavoidable, and the only remedy for deterioration in storage is to keep the moisture down. The result of bacterial deterioration in cotton is that the fibre is broken down when boiled with alkalis and a large part of it dissolves.

CHAPTER XV

BLEACHING PROCESSES

Bleaching without scouring—Use of volatile solvents in scouring—Bleaching by means of oxygen—Bleaching cotton for spinning.

Many methods of bleaching without boiling the goods have been from time to time suggested. For instance, Erban bleaches cotton by simply treating it with hypochlorite solutions containing Turkey-red oil. Higgins (*Journ. Soc. Chem. Ind.*, 1914, **9**, 92) made an investigation of these methods. 65·3 grms. of linen cloth, which were found to weigh 60·69 grms. when stove dry, were placed in 500 c.c. of water along with 3 per cent soda ash and ¾ per cent Turkey-red oil, and heated to 80° C. for two hours. The cloth was then rinsed, washed well, and the operation repeated, using a freshly prepared bath. It was again well washed and put into a solution of bleaching powder solution for four hours. By titrating the solution before and after the bleaching it was found that 2·87 grms. of "active" chlorine had been used up in the bleaching action. A similar piece of lime and lye boiled linen required only 0·55 grm. of chlorine to bleach it, so that to bleach by the steeping method would require more than five times the amount of bleaching powder that the ordinary method requires. Since bleaching powder is the most expensive chemical the bleacher uses, and represents a large proportion of the cost of bleaching, the bleaching powder required for the steeping method would make that process extremely costly; there is also the cost of the soda ash and Turkey-red oil to add. Even after the treatment described, the linen was still

yellow and unsuitable for any market. Moreover, on boiling and chemicing to produce a fair white, it lost a great amount in weight. It contained 0·32 per cent of wax, which is much greater than that contained by properly bleached linen, and the small gain in weight, at which the steeping process aims, had only been achieved by retaining much of the original non-cellulose constituents of the fibre. Higgins has shown (*Journ. Soc. Chem. Ind.*, 1911, **30**, 1295)[1] that the drop in weight during bleaching takes place during the boiling operations if the process is properly conducted, and the figures given above show that good boiling is the cheapest way of getting rid of the impurities of the cloth, besides being the only way to produce a good white.

Recently a number of substances have been introduced for adding to the scouring liquors in order to eliminate the waxy matters of the cloth. Benzene and liquids of similar properties are brought into an emulsion with water by means of Turkey-red oil, and, on adding these mixtures to the lye boils, they act very effectively in assisting the removal of the waxes and fatty matters. Higgins (*Journ. Soc. Chem. Ind.*, 1914, 902) found, however, that their cost did not admit of extensive adoption on the large scale.

Other bleaching processes are described in different parts of the book, *e.g.* pages 40 and 71. J. L. Jardine and J. A. Nelson (Eng. Pat. 802 of 1914) digest textile fibres under pressure with magnesium or sodium bisulphite, the gases liberated during the treatment being removed in order to prevent deterioration of the fibre by liberated sulphur dioxide. This treatment is recommended in place of the usual lime boiling and lime souring. J. M. Matthews (*Journ. Ind. Eng. Chem.*, 1911, **3**, 191-193) suggests that hydrogen peroxide is a safer and cheaper bleaching agent than sodium perborate, although the latter possesses the advantage of being capable of incorporation with soaps and washing powders. In bleaching with an alkaline peroxide a claim has been made (*Deutsche Gold und Silber-Scheide Anstalt.*, Eng. Pat. 10916, 1915) for heating the bath immediately to

[1] See page 31.

85° C. to produce a better white in a shorter time. To prevent the flocculation of calcium soaps in washing baths, the addition of a soluble colloid, *e.g.* glue, albumin, has been protected by Farbenfabr. von F. Bayer und Co. (Ger. Pat. 294028, 1914).

R. Müller (Fr. Pat. 414, 821, 1910) bleaches by means of the oxygen of the air in the following manner. The material is heated, preferably at a high temperature and under pressure, with the aqueous solution of the hydroxide of an alkali or an alkaline earth metal, through which a current of air or oxygen is being passed. The bleaching is accelerated if a small quantity of manganous carbonate is added to the solution. Later (addition dated November 5, 1910), in order to prevent over-bleaching, Müller finds it necessary to keep the cloth covered with the lye during the process. After heating for two hours, air being excluded, he directs a current of air on to the surface of the lye until the bleaching is completed. He then clears the manganese dioxide from the cloth by sodium sulphite. In a further addition (Ger. Pat. 242, 296, 1910) the alkaline solution, in which the goods are to be bleached, is allowed to circulate first over manganese dioxide in order to get the oxygen evolved more slowly. A company was formed to work this process in Germany, the mode of procedure being to add a small quantity of manganese sulphate to the caustic soda in the kier, boil for two hours, and then admit air at a pressure of $3\frac{1}{2}$ atmospheres. After boiling for twelve hours with the admission of air it is asserted that the goods are completely bleached, no subsequent chemicing being necessary. A considerable saving of time and chemicals is claimed. The method is ideal from the chemical standpoint, but the present author thinks that its survival is doubtful, because of the risk of tendering. A method might be very scientific and economical, but, if it results in an occasional lot of goods being tendered, the economy of the process disappears, and the process cannot survive. In fact, methods which require careful scientific control in order to prevent tendering do not commend themselves to bleachers; methods which are not risky and can be entrusted to workmen not scientifically trained are preferred.

In a process patented by J. Korselt (Ger. Pat. 287, 240, 1913) bleaching is carried out by a solution of hypochlorite of gradually increasing concentration. This process is said to prevent irregularities causing the formation of oxycellulose, noticeable when hypochlorites of gradually decreasing concentration are used, to produce an improved fibre with the retention of the spinning properties, and to give an excellent white with a very small loss in weight. It cannot, however, be an economical process, because, as has already been pointed out (p. 121), scouring is a cheaper way of eliminating impurities than treatment with hypochlorite solutions, and because a large amount of the strong hypochlorite will be retained by the fibre and lost in the subsequent washing.

A. Poulsen (Eng. Pat. 104048, 1916) bleaches loose fibres and other materials by boiling in a mixture of sodium carbonate and bicarbonate, then treating with sodium hypochlorite solution, while H. R. Anders (U.S. Pat. 1251614, 1918) uses lime for the boiling, and lime and a "substance carrying oxygen" for the bleaching.

CHAPTER XVI

BLEACHING FAULTS

Paraffin wax stains—Mineral oil stains—Pink stains on white cloth—Black stains—Lead stains—Kier damages—Damages due to metallic particles—Alloy resistant to hypochlorites.

PARAFFIN wax is often used in sizing mixings, the object being to lubricate the sized threads for the weaving process. Tallow is the proper substance to use for this purpose, but paraffin wax is used either consciously because it is cheaper or unconsciously in the form of adulterated tallow. F. Whowell (*Textile Inst. Journ.*, 1911, **2**, 43-53) points to the trouble caused by this substance in bleaching. Paraffin wax and similar unsaponifiable substances are not emulsified in the boiling processes to which the goods are submitted preparatory to bleaching or dyeing. The wax is simply loosened, floats on the top of the kier, and settles on the goods in the form of patches, producing grey water-resistant stains which cannot be bleached or dyed. Sometimes the wax remains evenly distributed over the cloth without forming patches, in which case the fibres remain absolutely resistant to the calendering operation, and the cloth finishes up limp. Mineral oil stains derived from the lubricating oil of the looms or other machinery are likewise objectionable, and it has been clearly demonstrated that mineral oil stains resist all known processes of bleaching, but it would appear that a mixture of vegetable and mineral oil is not so harmful.

A. Scheurer (*Bull. Soc. Ind. Mulhouse*, 1910, **80**, 343) found that the treatment with lime then caustic soda lyes containing resin removed stains produced by a 1 per cent solution of paraffin wax in benzene; the stains were, in

fact, removed to the extent of three-quarters their area, the remainder forming a ring, in the centre of which was a portion which was wetted by water. Stains produced by a benzene solution of tallow and paraffin were completely removed, but if the paraffin exceeded 5 per cent of the mixture of tallow and paraffin the stains were not removed. The author points out that mineral oils contain varying amounts of non-volatile substances and that these are the only source of stains from lubricating oils of any importance. Fresh stains of Scotch petroleum were almost completely removed by cleaning, whilst, if the stained fabric had been exposed to the air for some time beforehand, the stains are much less completely removed. A. Scheurer and E. Wallach (*Bull. Soc. Ind. Mulhouse*, 1913, **83**, 510-608) found, of all the constituents of mineral oil, paraffin was the most harmful. No mineral oil could be found which did not stain, but non-staining preparations could be obtained either by mixing with mineral oil a vegetable oil which did not emulsify easily in scouring, or by using an emulsifiable mineral oil. The former method is the one recommended, and the mixture must contain at least 60 per cent of the vegetable oil. A mixture of 75 per cent of colza oil with 25 per cent of mineral oil gives the best results. Vegetable oils have the drawback of costliness and tendency to clog. The use of emulsifiable mineral oils would appear to be a better solution of the problem, but at the present time such of these as are on the market are not manufactured with the present object in view, and, as they vary in quality, cannot be recommended. L. Lefèbre (*Rev. Gen. Mat. Col.*, 1910, **14**, 341) states that the addition of sulphoricinoleate of sodium or sodium oleate to the caustic lyes used in the boiling process, as recommended by Scheurer (*Journ. Soc. Chem. Ind.*, 1903, 1344), removes stains which contain 33 per cent of mineral oil, but if the quantity exceeds 50 per cent the stain still remains after bleaching.

This removal of stains must be considered along with the removal of waxes described on p. 38, and also in the light of Shorter's work on emulsification (p. 40).

S. J. Pentecost (*Journ. Soc. Chem. Ind.*, 1909, **28**, 1180) states mineral oil stains penetrate the cuticle of the

fibre and, on finishing, the oil oozes out from the interior of the fibre, causing a yellow stain. He also describes a pink stain found on the edges of cotton pieces, which he proved to be due to the attraction of aniline vapour by the cotton and its oxidation in the air to a mauveine. Recently the present author has come across a pink stain in cotton goods which had been developed during shipping. Without knowing of Pentecost's paper he found that the pink colour was due to aniline, and concluded that the goods must have been at some period in aniline vapour. He once used aniline oil to take out a peculiar tar stain from finished goods, and found the same pink stain produced on white goods in the immediate neighbourhood. Then all organic chemists know the brown to pink colour of the paper of text books, etc., which are used in the organic laboratory, this colour being due to the attraction and oxidation of aniline vapour.

S. R. Trotman (*Journ. Soc. Chem. Ind.*, 1909, **28**, 1237) mentions a pink stain similar to the one described by Pentecost but produced by the growth of a chromogenic mould. The colonies consisted of very fine mycelia which were closely attached to the surface of the medium and which only produced colourless aerial hyphae carrying sporangia, after an interval of nearly a fortnight. A second batch of goods developed the colour while standing after the soda boil, and it was probable that this was the point of infection. The organism or its spores were capable of withstanding the chemic and acid, and subsequently developed under the influence of the warmth of the warehouse. He emphasised the necessity to prevent such growths of using pure water for steeping, good scouring to get rid of the nitrogenous bodies in the cloth, careful handling in the wet state, the use of pure finishing materials, and careful storing of finished goods.

Higgins (*Jour. Soc. Chem. Ind.*, 1911, **30**, 188) describes black stains produced by a blueing mangle owing to the reaction of the copper on the brass bowl with mercuric chloride used as an antiseptic in the starch. Mercury in finely divided state was liberated by the copper and produced black stains on the cloth going through the mangle.

W. H. Pennington (*Journ. Soc. Dyers and Col.*, 1907, **25**, 46-47) found lead stains were produced by the conversion of the lead of lead-lined wooden cisterns into red lead by bleaching powder solution. The stains were dark brown. Other cases of lead stains were produced (1) by a lead pipe through which bleaching powder flowed; (2) by contamination with a leaden floor; (3) production of lead sulphide in the kier from (*a*) a leaden plate in the top of the kier and (*b*) headings dyed with chrome orange.

Other damages have been mentioned in the body of the book, such as those produced by metallic oxides (p. 56).

J. F. Briggs (*Journ. Soc. Chem. Ind.*, 1916, **35**, 78), in discussing damages in bleaching, mentions that warp and weft yarns may not be adapted to one another, as when, for the sake of cheapness, a very loosely spun weft is combined with a warp containing strips of hard twisted 2-ply yarn. Under the friction of use the hard warp may disintegrate the loosely twisted weft, and the unexpectedly short life of the latter may be attributed to the yarn bleacher. Kier damage, due to the exposure of the cloth above the boiling liquor, is produced both in lime and lye boiling and occurs in the form of patches, several inches across, of tender but not absolutely disintegrated cloth, merging gradually into sound material. There is no evidence of the formation of oxycellulose. By some chemists this damage is attributed to the concentrated action of the boiling alkali, through the drying up of the exposed portions; by others to the oxidising action of the air in the steam. The crystallisation of calcium carbonate in the fibre may cause a mechanical damage. The cellulose shows no chemical alteration, but under the microscope the structure is seen to be profoundly affected. When a deposit of lime is formed locally in the cloth, *e.g.* by the drying of exposed portions in the lime boiler, calcium carbonate may be formed inside the fibre. Cloth showing such stains may be quite tender; the linen fibres when examined microscopically will then show a large number of "kinks" or bursts resembling somewhat the "nodes" of bamboo.

The production of faults due to metallic oxides has been pointed out by Higgins (*Journ. Soc. Chem. Ind.*, 1911, **30**, 188). The bleacher of heavy linens finds from time to time that bleached goods contain damages which are like cuts with a sharp knife; sometimes a piece is cut almost in two by this fault. In most cases the yarn, generally a warp yarn, is the cause of the trouble, and on separation this yarn is found to be black and to contain oxycellulose. The black substance was found to be copper oxide, and the contamination was caused by oil, which contained some copper from the brass parts of the machinery used in the production of the cloth or yarn. The copper oxide caused the rapid evolution of oxygen from the bleaching powder solution when the goods were in the bleaching bath, and this excessive local evolution caused the tendering of the fibre in the parts adjacent to the oxide. J. F. Briggs (*Journ. Soc. Chem. Ind.*, 1911, **30**, 397) agreed that the fault was caused by the contamination of oil containing copper, but attributed the tendering to metallic copper not copper oxide. Higgins (*Journ. Soc. Chem. Ind.*, 1911, **30**, 1296) showed that copper oxide had a far greater effect in causing the evolution of oxygen from bleaching powder solution than metallic copper had. In fact, the metal was oxidised to the oxide before it acted. Similarly iron and nickel were oxidised before acting on bleaching powder solution, and iron rust caused holes in linen cloth during the action of bleaching powder solution. He also pointed out that zinc, like aluminium, caused the evolution of hydrogen from bleaching powder solution so that zinc would have no tendering action like copper has. W. Thomson (*Journ. Soc. Dyers and Col.*, 1914, **30**, 142-143) experimented with cloth on which varying amounts of chromium oxide had been fixed and showed that bleaching powder solution produced a degree of tendering roughly proportional to the amount of chromium on the fibre. This tendering action of chromium had previously been mentioned by Higgins (*Journ. Soc. Dyers and Col.*, 1913, **29**, 85) (see p. 57). P. Weyrich (*Z. angew. Chem.*, 1915, **28**, 399) found that bleaching liquor acts on most metals, chromium, tin, lead and bismuth being the most resistant. Borcher's alloy, a chrome-

tungsten steel, is also very resistant. S. J. Pentecost (*Journ. Soc. Chem. Ind.*, 1918, 169 R.) states that some samples of nitre cake contain iron, which might cause trouble in the bleaching process in the way stated above, and P. Heermann (*Chem.-Zeit.*, 1918, **42**, 85-86) points to the occurrence in small quantities of metallic salts, *e.g.* of copper and iron, in stains on linen and cotton goods, which produce tendering in the manner described above. Perborates and washing powders containing available oxygen will in some cases produce perforation and destruction of the fabrics.

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